STANDARDS DEVELOPMENT BRANCH OMOE
36936000003648

NANTICOKE WATER QUALITY STUDY

1969—1983

MAIN REPORT

WATER RESOURCES BRANCH
MINISTRY OF THE ENVIRONMENT

TD
227.E75
057
1986
MOE

TD
227.E75
O57
1986

Nanticoke water quality study
1969-1983 : main report /
24262

Copyright Provisions and Restrictions on Copying:

This Ontario Ministry of the Environment work is protected by Crown copyright (unless otherwise indicated), which is held by the Queen's Printer for Ontario. It may be reproduced for non-commercial purposes if credit is given and Crown copyright is acknowledged.

It may not be reproduced, in all or in part, part, for any commercial purpose except under a licence from the Queen's Printer for Ontario.

For information on reproducing Government of Ontario works, please contact Service Ontario Publications at copyright@ontario.ca

Ref - 24262

NANTICOKE WATER QUALITY STUDY

1969-1983

MAIN REPORT

Prepared for

GREAT LAKES SECTION
WATER RESOURCES BRANCH
MINISTRY OF THE ENVIRONMENT
135 St.Clair Ave. W.
Toronto, Ont.
M4V 1P5

by

ACRES INTERNATIONAL LIMITED
5259 Dorchester Road
Niagara Falls, Ont.
L2E 6W1

March, 1986

STANDARDS DEVELOPMENT BRANCH
135 ST. CLAIR AVENUE WEST
TORONTO, ONTARIO M4V 1P5

TABLE OF CONTENTS

LIST OF TABLES
LIST OF FIGURES

Page

1 - INTRODUCTION ---------- 1

2 - METHODS ---------- 5
2.1 - Study Area ---------- 5
2.2 - Monitoring Network ---------- 8
2.3 - Sample Collection ---------- 10
2.4 - Sample Analysis ---------- 15
2.5 - Data Analysis ---------- 15
2.5.1 - Data Summary ---------- 17
2.5.2 - Areal Homogeneity ---------- 18
2.5.3 - Provincial Water Quality Objective Exceedances ---------- 19
2.5.4 - Trend Analysis ---------- 21
2.5.5 - Loadings ---------- 30
2.5.6 - Correlations ---------- 32
2.5.7 - Metals Statistics ---------- 34

3 - RESULTS ---------- 38
3.1 - Data Summary ---------- 38
3.2 - Areal Homogeneity ---------- 39
3.3 - PWQO Exceedance ---------- 45
3.4 - Trend Analysis ---------- 59
3.5 - Loadings ---------- 67
3.6 - Correlations ---------- 71
3.7 - Metals Statistics ---------- 74
3.8 - Trophic Conditions ---------- 77

4 - DISCUSSION ---------- 81
4.2 - Data Quality ---------- 81
4.1.1 - Interlaboratory Comparison ---------- 81
4.1.3 - Internal Quality Control ---------- 84
4.2 - Effects of Industrial Development at Nanticoke ---------- 87
4.3 - Recommendations for Future Work ---------- 87

5 - CONCLUSIONS ---------- 90

BIBLIOGRAPHY

APPENDIX A - NANTICOKE WATER QUALITY ANNUAL STATISTICS
APPENDIX B - NANTICOKE WATER QUALITY MONTHLY STATISTICS
APPENDIX C - TREND ANALYSIS

LIST OF TABLES

Number	Title
1	Nanticoke Water Sampling Stations
2	Nanticoke Sampling Station (by year) and Depths (metres)
3	Numbers of Visits to each Station, 1969 to 1983
4	Numbers of Water Quality Measurement Reported, 1969 to 1983
5	Parameters in Combined, Standardized Data Sets
6	Availability of Data for Trend Analysis
7	Summary of Input Data for Correlation Analysis
8	Parameters for Which Pairs of Stations Cluster Most Closely, 1969 to 1978
9	Parameters for Which Pairs of Stations Cluster Most Closely, 1981 to 1983
10	Numbers of Valid Measurements Comparied with PWQO
11	Trends in Monthly Median Values by the Seasonal Mann-Kendall Test
12	Significance Levels of Combined Kendal Tests for Trend
13	Mann-Kendall Trend Test on Estimatd Annual Values
14	Comparison of Shallow (X) and Deep (Y) Values
15	Comparison of Means Between and Within Samples
16	Composite Trophic Indexes for 1982-1983
17	Results of Some Interlaboratory Comparison Studies on Water Samples from the Lower Great Lakes
18	Inorganic Trace Contaminants Laboratory Results in Interlaboratory Studies on Water Samples

List of Tables - 2

19 Inorganic Trace Contaminants Laboratory Quality Control Results for Water Samples

20 Recent Trends in Eastern Basin Water Quality Compared with Trends at Nanticoke Stations

LIST OF FIGURES

Number	Title
1	Long Point Bay and Vicinity
2	Sampling Stations
3	Data Processing Flow Chart
4	Dendrograms for 1969-1978 Data
5	Dendrograms for 1981-1983 Data
6	PWQO Exceedances - Field pH
7	PWQO Exceedances - Lab pH
8	PWQO Exceedances - Phenols
9	PWQO Exceedances - NH_3
10	PWQO Exceedances - Total P
11	PWQO Exceedances - Cd
12	PWQO Exceedances - Cr
13	PWQO Exceedances - Cu
14	PWQO Exceedances - Fe
15	PWQO Exceedances - Ni
16	PWQO Exceedances - Pb
17	PWQO Exceedances - Zn
18	Industrial and Tributary Annual Loadings
19	Nanticoke Creek Annual Discharges and Loadings

List of Figures - 2

20	Correlation Matrix
21	Fit of Trace Metal Data to Lognormal Distribution
22	Comparison of Trace Metal Sample Means

1 - INTRODUCTION

In the 1970s, significant industrial development occurred at Nanticoke, Ontario (see Jeffs, 1981). Ontario Hydro constructed a 4000-MW fossil-fueled thermal generating station, which first generated electricity in January 1972. Texaco Canada Inc. (Texaco) built an oil refinery with a capacity of 15 000 m^3/d, which began operations in November 1978. The Steel Company of Canada Limited (Stelco) constructed a steel mill with an initial capacity of 1.2×10^6 t/yr and with the potential to expand to 10×10^6 t/yr. This mill began operation in May 1980.

The Nanticoke Environmental Committee (NEC) was formed in 1968, after Ontario Hydro announced their plans for the Nanticoke thermal generating station. Initially the NEC consisted of representatives from Ontario Hydro, the Ontario Water Resources Commission (now the Ministry of the Environment, or MOE), and the Ontario Department of Lands and Forests (now the Ministry of Natural Resources, or MNR). Stelco joined the Committee later in 1968, and Texaco joined in 1969, after announcing their plans for development at Nanticoke.

The NEC assumed responsibility for environmental studies to assess the effects of industrial development at Nanticoke. Studies of the following were begun under the supervision of the NEC

- water temperature by Ontario Hydro
- nearshore currents by Ontario Hydro and MOE
- water quality by MOE
- phytoplankton by MOE
- zooplankton by MNR

- benthos by MOE
- aquatic macrophytes by Ontario Hydro
- fish by MNR.

The goal of the water quality program undertaken by MOE was to detect changes in nearshore Lake Erie water chemistry attributable to industrial development at Nanticoke. To achieve this goal, the MOE collected water samples from the Lake Erie nearshore zone at Nanticoke from 1969 through 1983. These samples were analyzed for a wide variety of water quality parameters. The present report discusses the statistical analysis of the water quality data generated during the 15 years of monitoring at Nanticoke.

The objective of this report is to determine, through a variety of statistical tests, whether industrial development has appreciably influenced nearshore Lake Erie water quality at Nanticoke. The statistical tests employed, along with the reason for each, are as follows.

- The 15 years of Nanticoke water quality data are summarized on an annual basis, and on a monthly basis, using simple descriptive statistics. This gives a summary in one report of the mass of data gathered during the monitoring program.

- The areal homogeneity of the data is tested by cluster analysis. This reveals groups of stations that are consistently similar in their water quality characteristics. Possible explanations for station groupings, such as distance from shore or proximity to a potential pollutant source, are considered.

- The water chemistry data are compared with Ontario Provincial Water Quality Objectives to determine whether

the frequency or magnitude of objective violation can be related to industrial development.

- The data are subjected to a variety of trend analysis tests to ascertain whether seasonal or long-term trends exist.

- Annual loadings of several parameters to Long Point Bay are estimated for the industries and tributaries at Nanticoke. The time series of annual loadings are examined for trends related to trends in nearshore water quality.

- The correlations between phytoplankton biomass, chlorophyll-a, and nutrients are examined to determine whether these parameters are related in the Nanticoke water quality data.

- Trace metal data from several years are tested for fit to the lognormal probability distribution and are compared to determine whether they came from the same population. Potential physical causes of observed variability are considered.

Water quality changes in the Nanticoke area might be related more to changes in the eastern basin of Lake Erie as a whole than to local industrial development. To evaluate this possibility, trends revealed by the statistical analysis of the Nanticoke data are compared qualitatively with trends reported elsewhere for the eastern basin.

Finally, the quality of data generated by the MOE laboratory is discussed in relation to the quality of data from other analytical laboratories. Particular emphasis is placed on interlaboratory and intralaboratory variability and biases in trace metal data.

Following this introduction, the present report describes the methods used to collect and analyze Nanticoke water samples and to analyze the ensuing data. The data from the 15 years of monitoring are then summarized and the results of the above statistical analyses and qualitative comparisons are presented. Finally, conclusions of the report are given in summary form.

2 - METHODS

2.1 - Study Area

Lake Erie consists of three basins: eastern, central and western. From the north shore of the eastern basin, a long sand spit extends southeastward for over 40 km (Figure 1). This spit is called Long Point and the water between the spit and the north shore of Lake Erie is called Long Point Bay. The town of Nanticoke is situated on the north shore of this bay, about 10 km east of Port Dover. Ontario Hydro's generating station and Texaco's oil refinery are just east of Nanticoke and Stelco's steel mill is immediately to the west of the town.

Two streams flow through the Nanticoke industrial park and discharge into Lake Erie (Figure 2). The gauged portion of Nanticoke Creek drains an area of 181 km^2 and has an annual average discharge on the order of 1 to 2 m^3/s. Centre Creek drains an area of 12 km^2 and is ungauged.

The main emissions from the thermal generating station are gaseous and particulate by-products of combustion, ash from consumed fuel, and heated condenser cooling water (Jeffs, 1981). The maximum cooling water intake rate is 154 m^3/s and the maximum temperature rise of cooling water is kept to 8.3°C by pumping tempering water from the forebay to the discharge channel at rates of up to 64 m^3/s. An ash lagoon receives fly ash, bottom ash, wastewater from backwashing of filters and regeneration of ion exchangers, drainage from coal piles, and effluent from sewage treatment lagoons. Overflow (0.4 m^3/s) from the ash lagoon is released into the cooling water discharge channel.

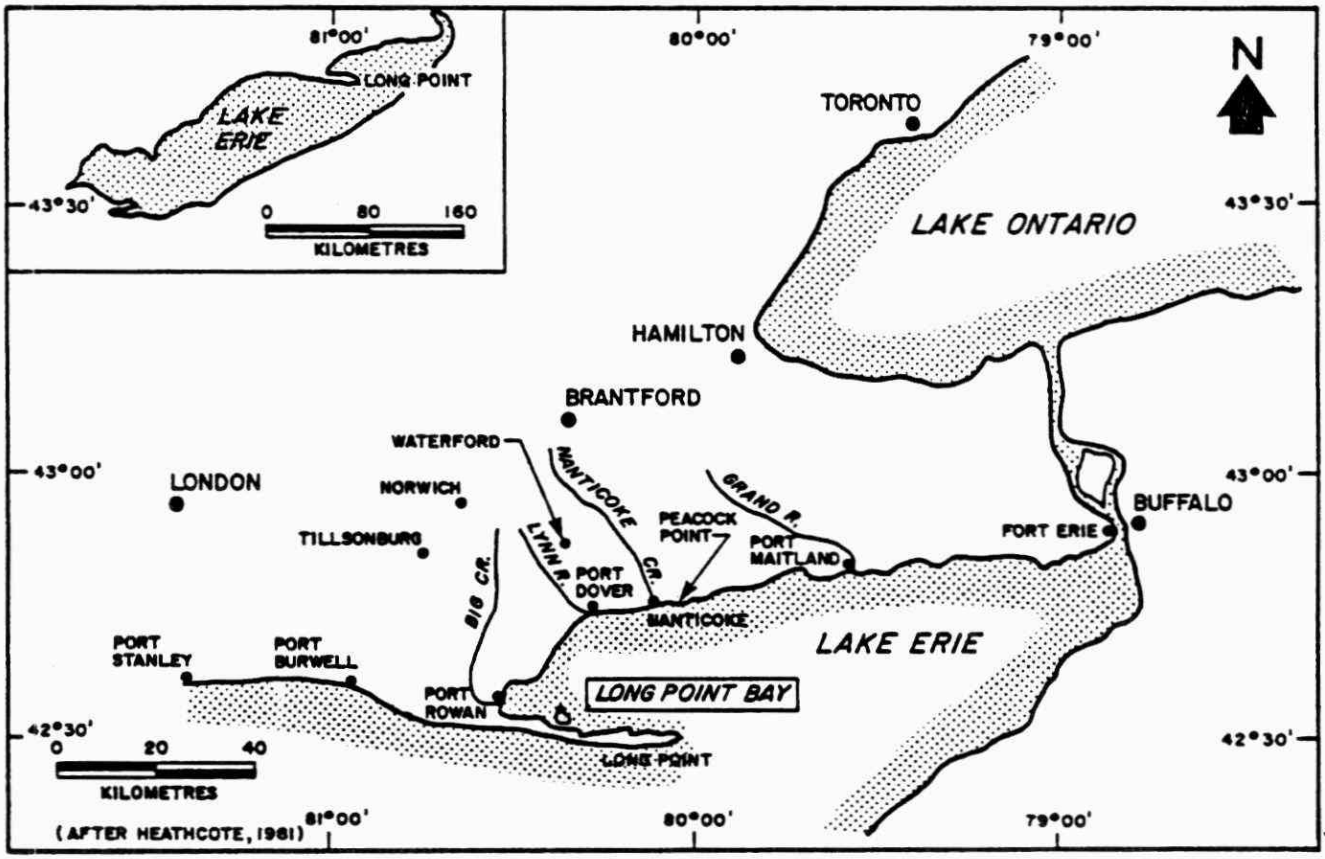


FIG. 1

MINISTRY OF THE ENVIRONMENT
NANTICOKE WATER QUALITY

LONG POINT BAY AND VICINITY

ACRES

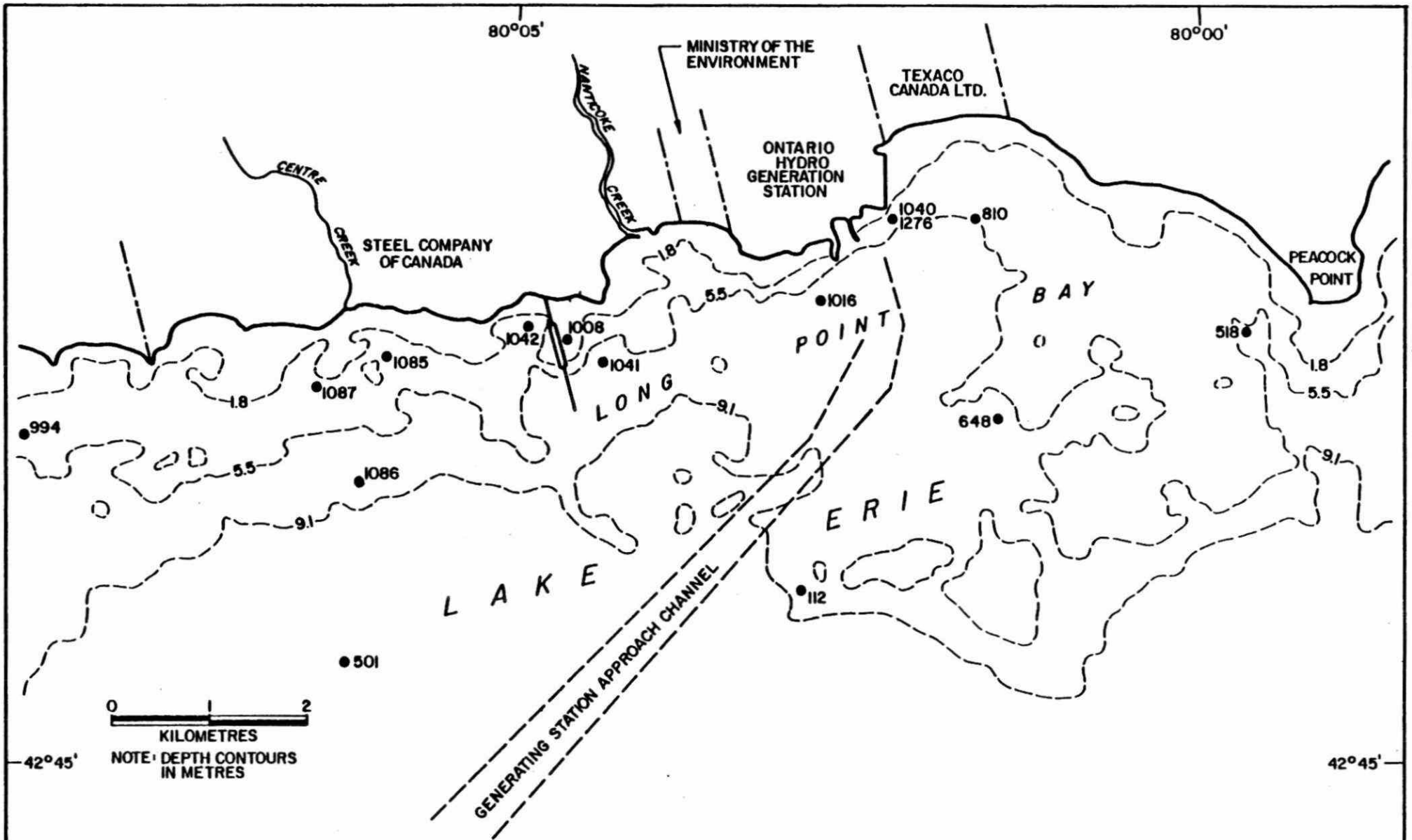


FIG. 2

MINISTRY OF THE ENVIRONMENT
NANTICOKE WATER QUALITY

SAMPLING STATIONS

ACRES

SOURCE: WEILER AND HEATHCOTE, 1979

The oil refinery uses cooling water at a rate of 460 to 650 m^3/d (Jeffs, 1981). Effluent from the wastewater treatment facility (less than 0.1 m^3/s) is monitored for compliance with discharge specifications and released into the lake through a submerged diffuser designed to achieve 10:1 dilution within 15 m of the ports in still water.

The steel mill needs process water at a rate of 7.6 m^3/t (Jeffs, 1981). Each of the several wastewater streams is given appropriate treatment and passed to a settling lagoon. The design discharge of this lagoon is 0.2 m^3/s and the effluent should meet Provincial Water Quality Objectives at the edge of a limited use zone extending a maximum of 1.5 km from the outfall.

Lake currents in the study area flowed parallel to shore about 64% of the time during the period 1967 to 1978 (Weiler and MacGregor, 1984). Eastward currents were 4 to 8 times more frequent than westward currents, depending on the distance from shore.

2.2 - Monitoring Network

A water sampling and statistical analysis study was done in 1968 to design the Nanticoke water quality monitoring program (Palmer, 1968). Conclusions of this study were that sampling stations in the area should be 3 km apart and that they should be sampled at approximately the same time of day on each sampling cruise. As a result of this study, a sampling network was established (Figure 2 and Table 1) and water quality monitoring began in 1969.

The original monitoring network consisted of eight stations. Stations 112, 501 and 648 were considered 'offshore' stations

TABLE 1

NANTICOKE WATER SAMPLING STATIONS

Station Number	Latitude (N)	Longitude (W)	Total Depth* (m)
112	42°45'55"	80°02'57"	12.3
501	42°45'32"	80°06'18"	11.3
518	42°47'18"	79°58'40"	5.5
648	42°46'50"	80°01'30"	7.6
810	42°47'54"	80°01'40"	8.5
994	42°46'45"	80°08'40"	7.7
1008	42°47'17"	80°04'36"	6.3
1016	42°47'28"	80°02'48"	9.9
1040	42°48'00"	80°02'00"	6.2
1041	42°47'08"	80°04'24"	9.8
1042	42°47'19"	80°04'57"	4.5
1085	42°47'17"	80°05'50"	3.2
1086	42°46'50"	80°05'55"	6.3
1087	42°47'10"	80°06'27"	3.4
1276	42°47'54"	80°02'06"	8.0

*Arithmetic means of total depths reported for all years of monitoring at each station.

and each was usually sampled at two depths: near surface and near bottom. Stations 518, 810, 1008 and 1016 were considered 'nearshore' stations. Stations 518 and 1008 were sampled at a depth approximately midway between surface and bottom. Stations 810 and 1016 were usually sampled near the surface and near the bottom. Finally, Station 994 was considered a 'control' station. This station was generally sampled near the surface and near the bottom.

Seven stations were added to the original eight in later years of the program. In 1971, Station 1040 was added as a nearshore station sampled at middepth. In 1975, Stations 1041 and 1042 replaced Station 1008 because Stelco's dock was built over the location of Station 1008. Stations 1085, 1086 and 1087 were added in 1978 to permit assessment of the effects of Stelco's treated effluent on water quality near the mouth of Centre Creek. Station 1276 was sampled in 1980 at middepth.

Table 2 lists the stations and depths sampled during each year of the program. Table 3 gives the numbers of visits to each station in each year. Table 4 shows the total number of measurements reported for each water quality parameter in each year.

2.3 - Sample Collection

A plastic Van Dorn bottle was used to obtain grab samples of lake water. Water samples were drawn from the Van Dorn bottle into specially prepared sample bottles provided by MOE's Laboratory Services and Applied Research Branch. The samples were preserved as specified in MOE (1981 and 1983) and shipped to the laboratory for analysis.

TABLE 2

NANTICOKE SAMPLING STATIONS (BY YEAR) AND DEPTHS (METRES)*

Station**	1969	1970***	1971***	1972***	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983
112	1	5.6	6.4	6.2	1	1	1	1	1	1	-	1	-	-	-
	12				11	12	11	11	11	11	-	10.5	-	-	-
501	1	5.1	6.2	6.2	1	1	1	1	1	1	1 - 1.5	-	1.5	1.5	1.5
	9				11	12	11	12	12	12	5.5-10.5	-	11	11	11
518	3	2.8	3.2	2.6	2.5	3	2.5	3	3	3	-	-	-	-	-
	-				-	-	-	-	-	-	-	-	-	-	-
648	1	3.6	4.0	3.6	1	1	1	1	1	1	-	-	-	-	-
	7				6	7	6	7	7	7	-	-	-	-	-
810	1	3.9	4.4	3.8	1	1	1	1	1	1	1.5	-	-	-	-
	8				7	8	7	8	8	8	-	-	-	-	-
994	1	3.0	3.5	3.8	1	1	1	1	1	1	-	1	1.5	1.5	1.5
	7				7	7	6	7	7	7	-	7	-	-	-
1008	3	3.0	3.2	3.1	3.4	3	-	-	-	-	-	-	-	-	-
	-				-	-	-	-	-	-	-	-	-	-	-
1016	1	4.6	5.1	4.9	1	1	1	1	1	1	-	-	-	-	-
	9				8.2	9	9	9	9	9	-	-	-	-	-
1040			2.9	4.0	3	1	3	3	3	3	1.5	-	-	-	-
					-	3	-	-	-	-	-	-	-	-	-
1041							1	1	1	1	-	-	-	-	-
							8	9	9	9	-	-	-	-	-
1042							2.5	2	2	2	-	-	-	-	-
							-	-	-	-	-	-	-	-	-
1085										1.5	1.5	1.5	1.5	1.5	1,5
										-	-	-	-	-	-
1086										1	-	1	1.5	1.5	1.5
										5.5	-	5.5	-	-	-
1087										1	1.5	1.5	1.5	1.5	1.5
										5.5	-	-	-	-	-
1276												1.5	-	-	-

* Information for 1969 to 1978 was reproduced from Table 1 of Weiler and Heathcote, 1979.

** A blank space for a station in a given year means that the station had not yet been established. A dash (-) means that the station had been established, but was not sampled in that year.

***During these years, samples were taken at middepth. There was considerable variation in sampling depth between cruises and the value reported is the average sampling depth for the year.

TABLE 3

NUMBERS OF VISITS TO EACH STATION, 1969 TO 1983

Station*	1969	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983
112	9	9	8	9	6	10	15	25	13	11	-	18	-	-	-
501	8	7	8	9	6	10	15	25	13	20	29	-	18	20	21
518	7	8	8	9	7	10	15	17	13	11	-	-	-	-	-
648	6	8	8	9	7	10	15	17	13	11	-	-	-	-	-
810	7	8	8	9	7	10	15	17	13	20	17	17	-	-	-
994	10	10	10	9	7	10	15	17	13	11	-	18	18	18	20
1008	8	8	8	9	7	10	12	1	-	-	-	-	-	-	-
1016	7	9	8	9	7	10	15	17	13	11	-	17	-	-	-
1040			8	9	7	10	14	17	13	20	17	-	-	-	-
1041							12	17	13	11	-	-	-	-	-
1042							12	17	13	11	-	-	-	-	-
1085										11	18	18	18	17	20
1086										11	-	18	18	18	20
1087										11	20	18	19	19	19
1276												18	-	-	-

*A blank space for a station in a given year means that the station had not yet been established. A dash (-) means that the station had been established, but was not sampled in that year.

TABLE 4

NUMBERS OF WATER QUALITY MEASUREMENTS REPORTED, 1969 TO 1983

Parameter	1969	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983
Turbidity	0	0	0	0	98	143	137	306	203	237	99	159	105	100	116
Temperature, water	101	99	175	150	106	142	337	303	191	256	102	288	306	214	238
Secchi disk, depth	7	91	168	173	42	23	432	501	306	484	240	23	306	208	236
Residue, filtered	0	0	0	9	0	84	136	134	102	84	0	0	0	0	0
Residue, particulate	0	0	0	9	0	14	0	117	102	84	0	0	0	0	0
Dissolved oxygen	51	138	73	72	0	0	120	130	23	120	102	244	258	214	232
Conductivity, 25°C	92	69	74	80	98	129	137	152	170	264	102	162	105	100	116
pH field	101	67	3	0	0	0	0	0	0	42	70	5	258	212	237
pH (-log H+ concn)	0	0	63	70	90	142	117	110	81	54	0	103	71	0	0
Alkalinity, total	0	0	0	9	0	0	0	129	102	84	0	0	0	0	0
BOD, 5 day, total demand	0	0	0	18	9	0	0	134	85	84	0	0	0	0	0
Chloride, unfil. reac	0	18	65	79	95	144	137	154	187	266	99	0	0	0	0
Sulfate, unfiltered reactive	0	0	0	0	9	57	0	136	102	84	0	0	0	0	0
Phenolics, unfiltered reactive	101	40	46	72	76	130	121	136	102	115	47	162	105	0	0
Ammonium, tot, filter, reac	92	69	74	78	98	132	137	154	204	278	109	162	98	135	119
Nitrogen, tot.ing filter. reac	92	69	74	78	98	132	137	154	204	278	109	162	0	0	0
Nitrates, total, filter.reac	50	0	0	0	0	0	0	130	168	247	109	144	101	137	0
Nitrate, filtered reactive	101	69	74	78	98	132	137	0	0	0	0	0	0	0	119
Nitrogen, tot.Kjeldahl fil.tot	82	62	74	77	98	132	137	171	202	284	109	161	310	145	118
Kjeldahl, organic unfil.reac	82	62	74	77	98	132	137	154	202	278	109	161	98	133	118
Total N, Sum of NO_3, NO_2 and KJ	82	62	74	77	98	132	137	154	202	278	109	161	101	135	0
Chlorophyll-a, total	1	3	93	114	25	90	194	191	118	196	135	104	105	103	119
Chlorophyll-b, total	1	3	93	114	25	90	193	191	118	196	125	102	0	98	119
Phytoplankton Data	38	52	72	107	86	80	141	153	97	143	0	88	45	53	59
Silicates, unfiltered reactive	0	0	0	0	0	0	117	130	146	233	106	133	70	6	0
Phosphate, filtered reactive	101	69	74	77	98	131	137	154	204	278	108	162	97	6	0
Phosphorus, unfiltered total	101	69	73	74	98	132	136	307	218	284	109	162	310	144	119
Cadmium, unfiltered total	0	0	0	18	9	0	120	0	0	111	30	142	106	97	83
Chromium, unfiltered total	0	0	0	18	9	0	0	0	0	111	30	142	106	97	236
Copper, unfiltered total	0	0	0	17	9	0	120	0	0	107	30	133	106	97	237
Iron, unfiltered total	0	0	0	18	81	127	121	136	102	128	95	142	321	181	119

Table 4
Numbers of Water Quality Measurements Reported, 1969 to 1983 - 2

Parameter	1969	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983
Nickel, Unfiltered total	0	0	0	17	9	0	120	0	0	105	30	142	106	97	236
Lead, unfiltered total	0	0	0	18	9	0	120	0	0	111	30	142	106	97	237
Zinc, unfiltered total	0	0	0	17	9	0	120	0	0	111	30	142	106	97	237
Boron, unfiltered total	0	0	0	18	9	0	0	0	0	0	0	0	0	0	0
Mercury, unfiltered total	0	0	0	18	9	0	0	0	0	0	15	130	104	0	0
Vanadium, unfiltered total	0	0	0	8	9	0	0	0	0	0	0	0	0	0	0
Potassium, unfiltered reactive	0	0	0	9	0	0	0	0	0	0	0	0	0	0	0
Cobalt, unfiltered total	0	0	0	0	0	0	0	0	0	99	0	142	106	97	0
Residue, total	0	0	0	18	9	36	1	0	0	21	0	0	0	0	0
Solvent extractables	0	0	0	18	0	0	0	0	0	0	5	0	0	0	0
Chemical oxygen demand	0	0	0	18	9	0	0	0	0	0	0	0	0	0	0
Carbon, dissolved organic	0	0	0	18	9	0	0	0	0	0	0	0	0	0	0
Secchi disk, color	7	91	168	173	42	0	0	42	0	108	240	0	0	0	0
Cyanide, avail, unfil. reac	0	0	0	9	9	0	0	0	0	0	0	141	103	0	0
Fluoride, unfiltered, reactive	0	0	0	17	9	0	0	0	0	0	0	0	0	0	0
Nitrite, filtered, reactive	101	69	74	78	98	132	137	0	0	0	0	0	0	0	0
Sulfide, unfiltered, reactive	0	0	0	9	9	0	0	0	0	0	0	0	0	0	0

Temperature and dissolved oxygen concentration were measured in situ with a dissolved oxygen meter. Secchi disk transparency was measured with a black and white Secchi disk. In 9 of the 15 years of monitoring, pH was measured in the field with a pH meter.

2.4 - Sample Analysis

The Nanticoke water samples were analyzed by the MOE Laboratory Services and Applied Research Branch at their laboratory in Rexdale, Ontario. The analytical methods used are described in MOE (1981 and 1983).

2.5 - Data Analysis

Figure 3 is a flowchart of data processing for this study. The first row of blocks in this figure shows the data types. Subsequent rows indicate the steps in the data analysis procedure.

The Nanticoke data were available in two forms, in computer files and printed on paper. The data in computer files were

- nearshore Lake Erie water quality and phytoplankton densities for 1969 to 1983 in the MOE Sample Information System (SIS)

- Centre and Nanticoke Creeks water quality in the SIS

- Nanticoke Creek discharge for the Water Survey of Canada's (WSC) stream gauge 02GC022

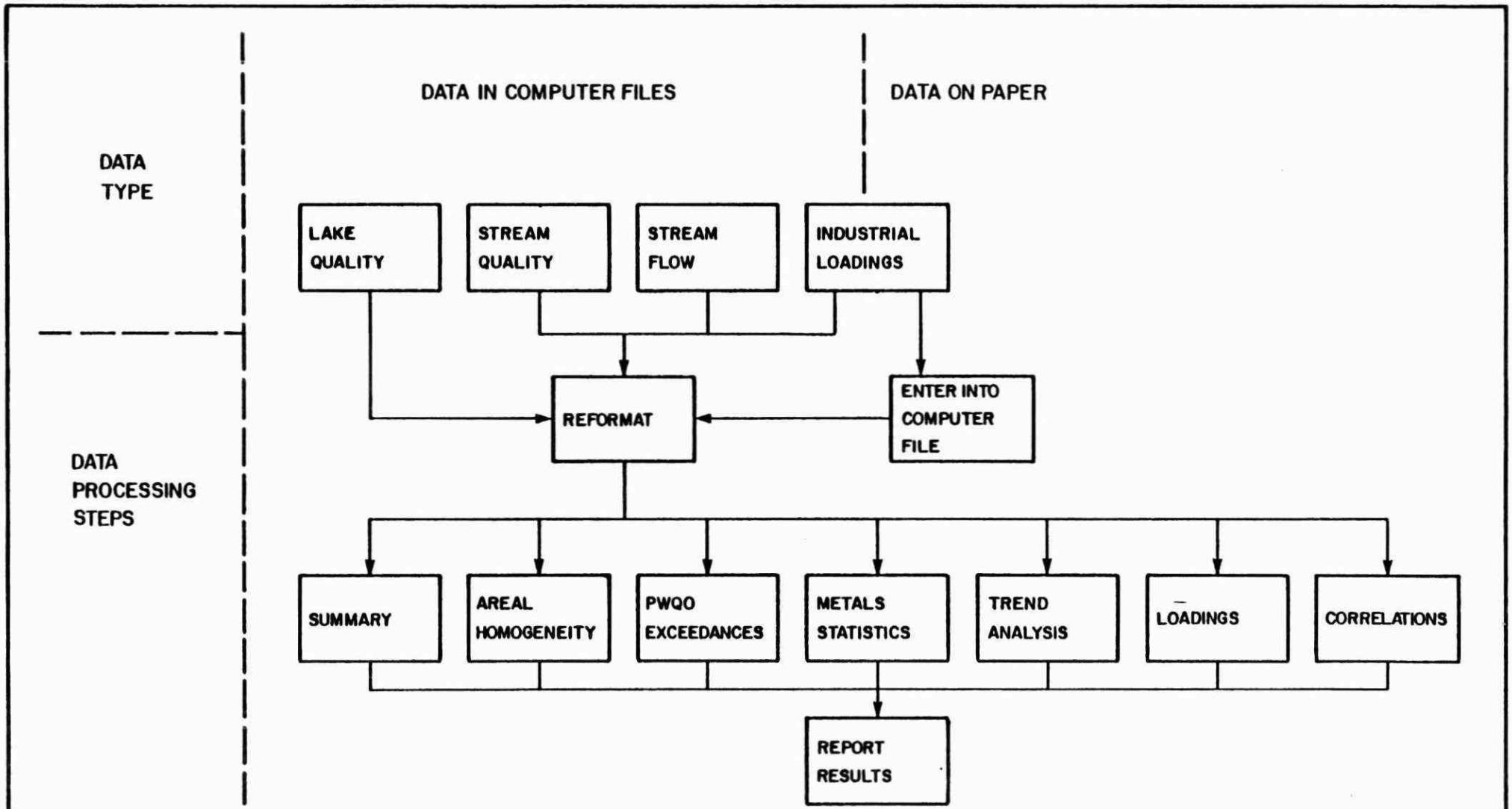


FIG. 3

MINISTRY OF THE ENVIRONMENT
NANTICOKE WATER QUALITY

DATA PROCESSING FLOW CHART

ACRES

- effluent loadings from the industries at Nanticoke for 1983 in the MOE Industrial Monitoring Information System (IMIS).

The data on paper were effluent flows, concentrations and loadings for the industries at Nanticoke for 1978 to 1982, held by Hamilton Region Office, West Central Region, MOE.

These data were obtained from their sources. Data received on paper were entered into Acres computer system manually. Data received on magnetic tape were copied into Acres system. The data sets, which were received in a variety of formats, were then transformed to formats compatible with existing data processing software.

2.5.1 - Data Summary

The water quality data for nearshore Lake Erie were described using a five-number summary: minimum, first quartile, median, third quartile, and maximum. These descriptive statistics were prepared for each parameter and each station in two ways

- on an annual basis, which gave a maximum of 15 five-number summaries for each parameter at each station, one summary for each year of monitoring

- on a monthly basis, in which all 15 years of data for a given parameter at a given station in a single month were described by 1 five-number summary. This gave a maximum of 11 five-number summaries, one for each month except January.

2.5.2 - Areal Homogeneity

The areal homogeneity of water quality in the study area was tested using cluster analysis. The method employed in this study computes a similarity measurement, such as the correlation coefficient or Euclidian distance coefficient, between all possible pairs of values in a data set and arranges the values into a hierarchy so the most similar values are grouped together. Then the groups, or clusters, of values are associated with other groups to which they are most similar. This procedure is repeated until all of the values have been placed in a comprehensive classification scheme.

The clustering method employed in this study was the weighted pair-group method with arithmetic averages (Davis, 1973). The distance coefficient was used as the similarity measure. The results were displayed in the form of a dendrogram, or tree diagram, which shows the relative similarities of the values.

The cluster analysis was done on two data sets. The first consisted of data for Stations 112, 501, 518, 648, 810, 994, and 1016 from the years 1969 to 1978. The stations in this data set were clustered on the basis of their levels of general parameters and nutrients. The second data set consisted of data from Stations 501, 994, 1085, 1086 and 1087 from the years 1981 to 1983. Stations in this data set were clustered on the basis of their levels of general parameters, nutrients, and trace metals.

Each analysis was done in two ways.

1 - First the stations were clustered for each parameter independently. The object was to find the pairs of stations that clustered most closely for each of the 34 most commonly measured parameters.

2 - Next, the data for several parameters were standardized by subtracting the mean and dividing the result by the standard deviation. The standardized data were combined into a single data set and the cluster analysis was repeated on this combined data set. The object was to find which stations were most alike on the basis of their levels of a variety of parameters. The parameters in the two combined, standardized data sets are given in Table 5. The differences between the two lists in this table were caused by a lack of simultaneous observations for a parameter in one data set or the other.

   In the cluster analysis, values reported as detection limits were assumed to be the detection limit.

2.5.3 - Provincial Water Quality Objective Exceedances

The MOE (1984) established Provincial Water Quality Objectives (PWQO) for the protection of aquatic life in Ontario's surface waters. Water quality data obtained from four stations during the Nanticoke water quality program were compared with these PWQO. Stations 501 and 810 were included in this comparison because they are the offshore and nearshore stations with the

TABLE 5

PARAMETERS IN COMBINED, STANDARDIZED DATA SETS

Parameter Name	Analyzed in 1969-1978 Data Set	Analyzed in 1981-1983 Data Set
Turbidity	X	X
Secchi disk depth	X	X
Residue filtrate	X	
Residue particulate	X	
Specific conductance	X	X
Alkalinity	X	
BOD_5	X	
Chloride	X	
Sulfate	X	
Ammonia	X	X
Nitrite + nitrate	X	X
Kjeldahl organic nitrogen	X	X
Chlorophyll-a	X	X
Phytoplankton biomass	X	
Reactive silicate	X	X
Reactive phosphate	X	X
Total phosphorus	X	X
Cadmium		X
Chromium		X
Copper		X
Iron	X	X
Nickel		X
Lead		X
Zinc		X

longest records. Station 994 was included because it had been designed as a control station. Station 1085 was included because of its nearness to the mouth of Centre Creek and the Stelco discharge.

Only 'valid' measurements were compared with the PWQO. Measurements reported by the analytical laboratory as suspect were not used. Similarly, measurements reported as having an actual value less than the detection limit were not used, unless the detection limit was less than the PWQO.

The number of PWQO 'exceedances' for each parameter at a sampling station in a year was determined as the number of valid measurements greater than or equal to (or perhaps less than or equal to in the case of pH) the PWQO. Then the percentage of measurements exceeding each PWQO was computed for each station in each year of monitoring.

For each PWQO exceedance, a dimensionless 'exceedance factor' was computed as the ratio of the measured value to the PWQO. Exceedance factors were computed only when an exceedance occurred, so the factor was always greater than or equal to 1.0.

For each sampling station in each year for which there is data, an arithmetic mean exceedance factor was calculated for each parameter.

2.5.4 - Trend Analysis

There are usually two main phases in a statistical study (Tukey, 1977). The first is an exploratory data analysis to discern important properties of the data using simple graphical and numerical techniques. The

second phase is a confirmatory data analysis to confirm statistically the presence or absence of certain properties of the data suggested by the exploratory data analysis. In this study, several exploratory and confirmatory data analysis techniques were used, as described below.

The trend analysis was done using data from five stations. Station 501 was included because it has the longest record of any of the offshore stations. Station 810 was included because it has the longest record of any of the nearshore stations. Station 994 was included because it was originally incorporated in the monitoring network as a control station. Stations 1085 and 1086 were included because they are the stations nearest Stelco's effluent discharge.

Data for 13 water quality parameters were subjected to trend analysis. The parameters, which were chosen both on the basis of their importance in water quality interpretation and on the length of their available record, were as follows.

- turbidity
- conductivity
- laboratory pH
- chloride
- total ammonium
- total inorganic nitrogen
- total Kjeldahl nitrogen
- Kjeldahl organic nitrogen
- chlorophll-a
- chlorophyll-b
- filtered reactive phosphate
- total phosphorus
- iron

Table 6 summarizes the availability of data for trend analysis.

Exploratory Data Analysis

A plot of the raw data against time constitutes one of the simplist and more useful exploratory graphical tools. Characteristics of the data that may be discovered in this plot include the following.

- extreme values
- trends
- known and unknown interventions
- seasonality
- need for a data transformation
- nonstationarity
- long-term cycles

Time series plots were prepared of the untransformed Nanticoke data.

Sometimes a time series plot obscures information in the data that a smoothed plot might reveal more clearly. The smoothed curve is constructed by dividing a time series into smooth and rough components and filtering out the rough, or noise, portion. The blurred 3RSR smooth (Tukey, 1977; McNeil, 1977) was used in this study. It was calculated for the average annual series that were estimated with the regression model described below, but only if the number of data points was greater than four. The bars in the blurred smooth plots are centred on the 3RSR smooth values, with the bar length equal to the magnitude of the median of the absolute value of all the roughs.

TABLE 6

Availability of Data
for Trend Analysis

Parameter	Station Number 501	810	994	1085	1086
turbidity	1973-1979 1981-1983	1973-1979	1973-1978 1980-1983	1978-1983	1978 1980-1983
Conductivity, 25° C	1969-1979 1981-1983	1969-1979	1969-1978 1980-1983	1978-1983	1978 1980-1983
Laboratory pH	1971-1978 1981	1971-1978	1971-1978 1980-1981	1978 1980-1981	1978 1980-1983
Chloride	1970-1979	1970-1979	1970-1978	1978-1979	1978
Ammonium, total	1971-1979 1981-1983	1971-1979	1971-1978 1980-1983	1978-1983	1978 1980-1983
Nitrogen, total inorganic	1973-1979	1973-1979	1973-1978 1980	1978-1980	1978 1980
Nitrogen, total Kjeldahl	1969-1979 1981-1983	1969-1979	1969-1978 1980-1983	1978-1983	1978 1980-1983
Kjeldahl organic nitrogen	1970-1979 1981-1983	1970-1979	1970-1978 1980-1983	1978-1983	1978 1980-1983
Chlorophyll-a	1971-1979 1981-1983	1971-1980	1970-1978 1980-1983	1978-1983	1978 1980-1983
Chlorohyll-b	1971-1979 1982-1983	1971-1980	1970-1978 1980 1982-1983	1978-1980 1982-1983	
Phosphate, filtered reactive	1970-1979 1981-1982	1970-1979	1970-1978 1980-1982	1978-1982	1978 1980-1982
Phosphorus, unfiltered total	1969-1979 1981-1983	1969-1979	1969-1978 1980-1983	1978-1983	1978 1980-1983
Iron, unfiltered total	1972-1979 1981-1983	1972-1979	1972-1978 1980-1983	1978-1983	1978 1980-1983

The box-and-whisker plot is a graphical presentation of the five-number summary described in Section 2.5.1. The lower and upper ends of the rectangle, or 'box', in the plot represent the first and third quartiles, respectively. The line drawn horizontally within the rectangle represents the value of the median. The minimum and maximum values are the end points of the lines, or 'whiskers', extending vertically from the rectangle.

Included on the box-and-whisker plot is an indication of 'outside' and 'far-outside' values. These are defined as follows (Tukey, 1977).

- The distance between the first and third quartiles is referred to as the 'H spread'.

- A step is 1.5 times the H spread.

- 'Inner fences' are one step outside the first and third quartiles and 'outer fences' are two steps outside.

- Values between an inner fence and its neighboring outer fence are called 'outside'.

- Values beyond outer fences are called 'far outside'.

Far-outside values were not included in the box-and-whisker plot if there were fewer than five data points in the set.

When there was an obvious lack of symmetry about the median in a box-and-whisker plot, the data were

transformed by the Box-Cox transformation to cause the data to be approximately normally distributed. This transformation is defined as (Box and Cox, 1964)

$$y_{ijk}^{(\lambda)} = \begin{cases} \lambda^{-1}(y_{ijk} + c)^{\lambda} - 1 & \lambda \neq 0 \\ \ln (y_{ijk} + c) & \lambda = 0 \end{cases}$$

where c is a constant that is usually assigned a magnitude just large enough to make all entries in the time series positive. The value of the Box-Cox parameter, λ, applied is included on the box-and-whisker plots. The value of λ was estimated by maximum likelihood.

Comparing box-and-whisker plots prepared for each season before and after the time of an environmental intervention can reveal the seasons in which the intervention caused noticable changes. At Nanticoke there have been two major environmental interventions, construction of the Ontario Hydro generating station and construction of the Stelco steel mill. The discharge from the Texaco oil refinery is quite small, so the intervention caused by construction of this facility was not considered.

The Ontario Hydro generating station came into operation in January 1972 and was phased into full operation over 5 years. Because few data are available from before 1972, January 1, 1976, was taken as the intervention date at which water quality near the generating station might have been affected. Of the five stations considered in the trend analysis, only Station 810 is close to the generating station. Thus, for each of the water quality parameters considered,

box-and-whisker plots were made for data from Station 810 from before and after the intervention date.

For the Stelco Mill, the intervention date was taken to be April 1, 1980. Box-and-whisker plots were prepared for data from Stations 501, 994, 1085, and 1086 from before and after the intervention date.

Confirmatory Data Analysis

The seasonal Mann-Kendall nonparametric test (Hirsch et al, 1982) was applied to detect possible trends in the data. This test is a multivariate extension of the Mann-Kendall test (Mann, 1945; Kendall, 1975). The resulting Mann-Kendall test statistic is positive for a monotonic upward trend with time and negative for a monotonic downward trend. For censored water quality time series, in which some data are reported as less than a detection limit, the affected data were fixed at a constant value less than the detection limit. Because nonparametric tests are based on ranks rather than magnitudes, all the censored values are interpreted as sharing the same rank, which is less than the rank of all the uncensored values. Monthly median values were used to compute the test statistics, which were calculated for each month across all the years for which data are available. Tests of hypotheses were also combined across seasons to arrive at an overall hypothesis test by Fisher's (1970) combination test and a combined score method (Hirsch and Slack, 1984).

Two tests were employed to check whether values reported for two different depths at the same time and location were significantly different.

- The Wilcoxon signed rank test (Wilcoxon, 1945; Conover, 1971) was used to check whether the values reported for two different depths at the same time have the same median.

- Pittman's (1939) test for equality of correlated variances was used to ascertain whether the variances of values determined simultaneously at shallow and deep depths are the same.

One-way analysis of variance (Sacks, 1984) and the Kruskal-Wallis test (Kruskal and Wallis, 1952) were employed to check whether the means among replicated samples are significantly different from each other.

A regression model was designed for determining the best data transformation, ascertaining the components required in a regression model, and estimating both the average monthly and annual values for the series. The most general form of this regression model is

$$y_{ijk}^{(\lambda)} = \mu + \mu_i + \alpha_j + \gamma_{ij} + \beta(x_{ijk}-\bar{x}) + e_{ijk}$$

where

$i = 1, 2, \ldots, n$ denotes the year

$j = 1, 2, \ldots, s$ denotes the season when there are s months per year (usually 9 because data were not available for January, February and March)

$k = 1, 2, \ldots, n_{ij}$ denotes the data point in the ith year and the jth season for which there are a total of n_{ij} data points

$y_{ijk}^{(\lambda)}$ is the kth data point in year i and month j where the λ indicates the Box-Cox transformation (Box and Cox, 1964) described above

μ - is the constant term

μ_i - is the parameter for the annual effect in the ith year

α_j - is the parameter for the seasonal effect in the jth season

γ_{ij} - is the interaction term

x_{ijk} - is the kth depth value for the ith year and jth season

$\overline{x}$ - is the mean depth across all the years and seasons

β - is the depth parameter

e_{ijk} - is the error for the kth data point in the ith year and jth season and is normally, independently distributed with mean zero and variance σ^2

In applying this model, the maximum likelihood estimate of the Box-Cox parameter, λ, was determined. If λ was not significantly different (at the 5% significance level) from 1.0, 0.0, -1.0, 0.5, or -0.5, the value statistically equivalent to λ was used to transform the data. Otherwise, the maximum likelihood estimate of λ was used to transform the data. The regression model was then fitted to the transformed data. Several goodness-of-fit measures were used to measure the

degree to which the objectives of model parsimony and good statistical fit were attained, including

- the Akaike information criterion (Akaike, 1974)

- Schwarz's (1978) approximation of the Bayes information criterion

- the square of the multiple correlation coefficient, R^2

The permutation test of Knuth (1969) was used to ascertain whether the residuals are random. Analysis of variance for the regression was used to compare the simplest possible regression model, for which there is only a mean level, to the full model, or to one or more reduced versions of the full model, to determine whether the simplest model could describe the data set statistically as well as the more complex models. A t statistic was used to test whether the depth parameter, β, is different from a constant value of zero.

After the regression model was fit to a data set, estimates were obtained for the average monthly values and average annual values. The Mann-Kendall test was then used to check whether the average annual values follow a monotonic trend.

2.5.5 - Loadings

The total mass of a substance introduced into a waterbody in a tributary flow in a specified time is referred to as the 'loading' of that substance. Annual loadings of several water quality parameters to Long Point Bay were estimated for industrial and creek discharges at Nanticoke.

Loadings from Stelco and Texaco were taken from reports submitted to MOE. These reports give estimates of average daily loading on a monthly basis. These average daily loadings were converted to monthly loadings, which were then summed to get annual loadings. The Texaco record extends from about mid-1978 through 1983. The Stelco record extends from about mid-1980 through 1983.

Available information on Ontario Hydro's loadings prior to 1982 was insufficient for loading calculations. The Ontario Hydro record thus covers only 1982 and 1983. The 1982 values are annual average loadings estimated by the MOE. The 1983 values are sums of monthly average loadings taken from the MOE IMIS.

Records of daily average discharges for Nanticoke Creek were obtained from the WSC (Gauge 02GC022). A discharge record for Centre Creek was synthesized by multiplying the Nanticoke Creek record by the ratio of the drainage area of Centre Creek to that of Nanticoke Creek (0.06). The result was a crude estimate of Centre Creek discharges that neglected any contribution from Stelco.

Water quality data for Nanticoke and Centre Creeks were obtained from MOE. These data were used along with the stream discharges to estimate annual loadings with the ratio estimator used by the International Joint Commission since 1976 for computing tributary loadings to the Great Lakes (Fraser and Willson, 1981). This method has been shown to be at least slightly better than several simple calculation schemes and flow concentration correlations at estimating loadings (Dolan et al, 1981). The loading estimator, u_y, is calculated by

$$u_y = \frac{u_x\,(m_y/m_x)[1+(1/n)(S_{xy}/m_x m_y)]}{[1+(1/n)(S_x 2/m_x 2)]}$$

where

u_x = mean daily flow for the year

m_y = mean daily loading for the days on which concentrations were determined.

m_x = mean daily flow for the days on which concentrations were determined

n = number of days on which concentrations were determined

$S_{xy} = [1/(n-1)]\,[\sum_{i=1}^{n} x_i y_i - n m_x m_y]$

$S_x 2 = [1/(n-1)]\,[\sum_{i=1}^{n} x_i^{\,2} - n\, m_x 2]$

x_i = individual measured flows

y_i = daily loading for each day on which concentration was determined.

Annual loadings for Nanticoke were analyzed for linear trends by least squares regression analysis. The loadings records for Centre Creek and the industries at Nanticoke were too short for meaningful trend analysis.

2.5.6 - Correlations

Data from Stations 501, 810, 994 and 1085 for phytoplankton biomass, chlorophyll-a, and nutrient concentrations were subjected to correlation analysis. For stations sampled near the water surface and near the bottom, only the near-surface data were used. For the purpose of correlation, concentrations measured for a

single day were assumed to be simultaneous measurements and the correlation analysis was done with zero lag.

The data to be correlated were extracted from the archive data files and placed into m x n arrays, with one array for each station. Each of the m rows contained the value recorded for each parameter for a single day. The columns were the n parameters to be correlated.

The correlation method used (Davis, 1973) requires that there be a value for every parameter on each day of sampling. Thus, any row having one or more missing values was omitted from the analysis. This requirement for a complete matrix of data considerably reduced the number of measurements suitable for correlation analysis. Several factors contributed to this reduction.

1 - Chlorophyll measurements were not taken in 1969.

2 - Occasionally a parameter was measured in the near-bottom sample but not in the near-surface sample.

3 - Changes in the monitoring program led to missing data for some parameters in some years.

The effect of these limitations in the data was examined by doing the correlation analysis on three different sets of input data (Table 7). The first set included data for all 10 of the parameters investigated. The second set included data for nine parameters. Reactive silicate, which was measured less often than the other parameters, was omitted. Also, when

data for nitrate plus nitrite were missing, nitrate data were included in data set 2 as an approximation to the nitrate plus nitrite concentration. This filled some of the gaps in the nitrate plus nitrite record. The chlorophyll data were omitted from the third data set, leaving just seven parameters to be correlated. Table 7 gives the number of observations of each parameter included in the three data sets used in the correlation analysis.

2.5.7 - Metals Statistics

Trace metal concentrations were measured extensively in only 4 years, 1980 to 1983. Data from these 4 years were tested for fit to a probability distribution and for whether data from different years at a single station are samples from the same population.

Water pollutant concentration data are typically positively skewed (Herricks et al, 1985). Thus the lognormal distribution generally gives a good statistical fit to water quality data. One researcher reported that of the 100 or so water quality data sets he has fit to a distribution, 85 to 90% were adequately fit by the lognormal distribution (D. Schaeffer, Illinois Environmental Protection Agency, personal communication, 1985).

Visual inspection of frequency plots of selected Nanticoke trace metal data sets showed that these data also appeared to be lognormally distributed. The approach adopted, therefore, was to test the null hypothesis that the trace metal data are lognormally distributed. With the assumption of lognormality, the problem posed by concentrations reported as detection limits could be circumvented as follows.

TABLE 7

SUMMARY OF INPUT DATA
FOR CORRELATION ANALYSIS

Parameter	Input Data Set Number* 1	2	3
Nitrogen, total inorganic	X	X	X
Nitrate + nitrite	X	X	X
Nitrogen, total Kjeldahl	X	X	X
Nitrogen, organic	X	X	X
Chlorophyll-a	X	X	-
Chlorophyll-b	X	X	-
Phytoplankton biomass	X	X	X
Silicate, reactive	X	-	-
Phosphate, reactive	X	X	X
Phosphorus, total	X	X	X
Number of observations			
for Station 501	21	32	41
810	19	30	40
994	34	47	61
1085	12	13	14

*X - indicates that data for this parameter were included.
- - indicates that data for this parameter were not included.

Trace metal data sets were prepared using data from near-surface samples collected in 1980 to 1983 at Stations 112, 501, 994, 1085, 1086 and 1087. Each data set consisted of concentrations of one parameter at one station in 1 year. Where there were replicate trace metal concentrations for a water sample, the geometric mean of the replicate concentrations was used. The values in each data set were arranged in ascending numerical order, then each data set was subjected to the following sequence of steps.

1 - The largest reported detection limit was determined.

2 - The lowest actual concentration above the detection limit was determined.

3 - The data were transformed to their logarithm to base 10.

4 - The median of the transformed data set was found. For a normal probability distribution, the median equals the mean. Consequently, the median of the transformed data was taken to be an estimate of the population mean of a normal distribution.

5 - If the mean was less than the lowest transformed actual concentration, computation was stopped. With half or more of the values below the detection limit, the data are not sufficient to determine the probability distribution.

6 - The transformed data values equal to or greater than the mean were used to compute the standard deviation of the transformed data.

7 - With these estimates of the population mean and standard deviation, the fit of the transformed data set to a normal probability distribution was tested by the χ^2 goodness-of-fit test.

The estimated population parameters for copper, iron and zinc data were compared to ascertain whether the data from different years for a given station represent different samples from the same population. A t-test for equality of means was used to make this comparison. Statistics for Stations 501, 994, 1085, 1086 and 1087 were used.

3 - RESULTS

3.1 - Data Summary

The results of the first 11 years of the Nanticoke water quality program were published in a series of reports issued by MOE (Palmer, 1970, 1971 and 1972; Polak and Kennedy, 1975; Polak, 1975, 1977, 1978a and 1978b; Heathcote, 1979; Tanner, 1981). In addition, reports summarizing the findings of the first 10 years of monitoring have been issued (Weiler and Heathcote, 1979; Heathcote et al, 1981).

The last year of monitoring was 1983. Reports for 1980 (Demal and Tanner) and 1981 (Amik) are in preparation and no reports have been prepared for 1982 and 1983.

The Nanticoke water quality data are summarized in Appendixes A and B to the present report. This summary takes the form of five statistics: minimum value, first quartile, median, third quartile, and maximum value. For data that are not normally distributed, which tends to be true of water quality data, these statistics give a better descriptive summary of the data than do the mean and standard deviation. Appendix A summarizes the data for each water quality parameter at each station on an annual basis. Appendix B summarizes the data on a monthly basis.

The remainder of this report is devoted to presentation of results of more complex statistical analyses of the Nanticoke water quality data.

3.2 - Areal Homogeneity

Two sets of data were subjected to cluster analysis. The first included data for seven stations from the first 10 years of monitoring. The second included data for five stations from the last 3 years of monitoring.

Each data set was analyzed in two ways.

1 - Stations were clustered separately for each parameter.

2 - Values for several parameters were converted to standard normal form and combined into a single data file which was then used to cluster the stations.

Table 8 shows the two stations that cluster most closely for each one of 26 parameters in the first (1969 to 1978) data set. The pair of stations that clustered most closely for the greatest number of parameters (7) was 518 and 810. These are both nearshore stations east of the Hydro generating station. Station 112 and 648 clustered most closely with each other for almost as many parameters (6) as did 518 and 810. Stations 112 and 648 are in deeper water directly offshore from the generating station. Another offshore station, 501, clustered most closely with Station 112 for several (4) parameters, suggesting that Stations 112, 501, and 648 are fairly similar.

Cluster analysis of the standardized, combined, 1969 to 1978 data results in two major clusters (Figure 4). One is a cluster of the three nearshore stations to the east of the generating station. The other consists of the three stations farthest offshore and the control station to the west of the mouth of Centre Creek. These results basically confirm the finding of Weiler and Heathcote (1979) that the Nanticoke

TABLE 8

PARAMETERS FOR WHICH PAIRS OF STATIONS CLUSTER MOST CLOSELY, 1969 TO 1978

Station	501	518	648	810	994	1016
112	RSF Dis. Oxygen chlor. a Fe		RSP sp. cond. Cl SO_4 $NO_2 + NO_3$ phosphate			
501			turbidity		alkalinity	
518			pH	temperature Secchi depth inorg. N NO_3 TKN total N		phytoplankton
648				Kjel.org. N chlor. b		NH_3 silicate
810		total P			BOD_5	
994						

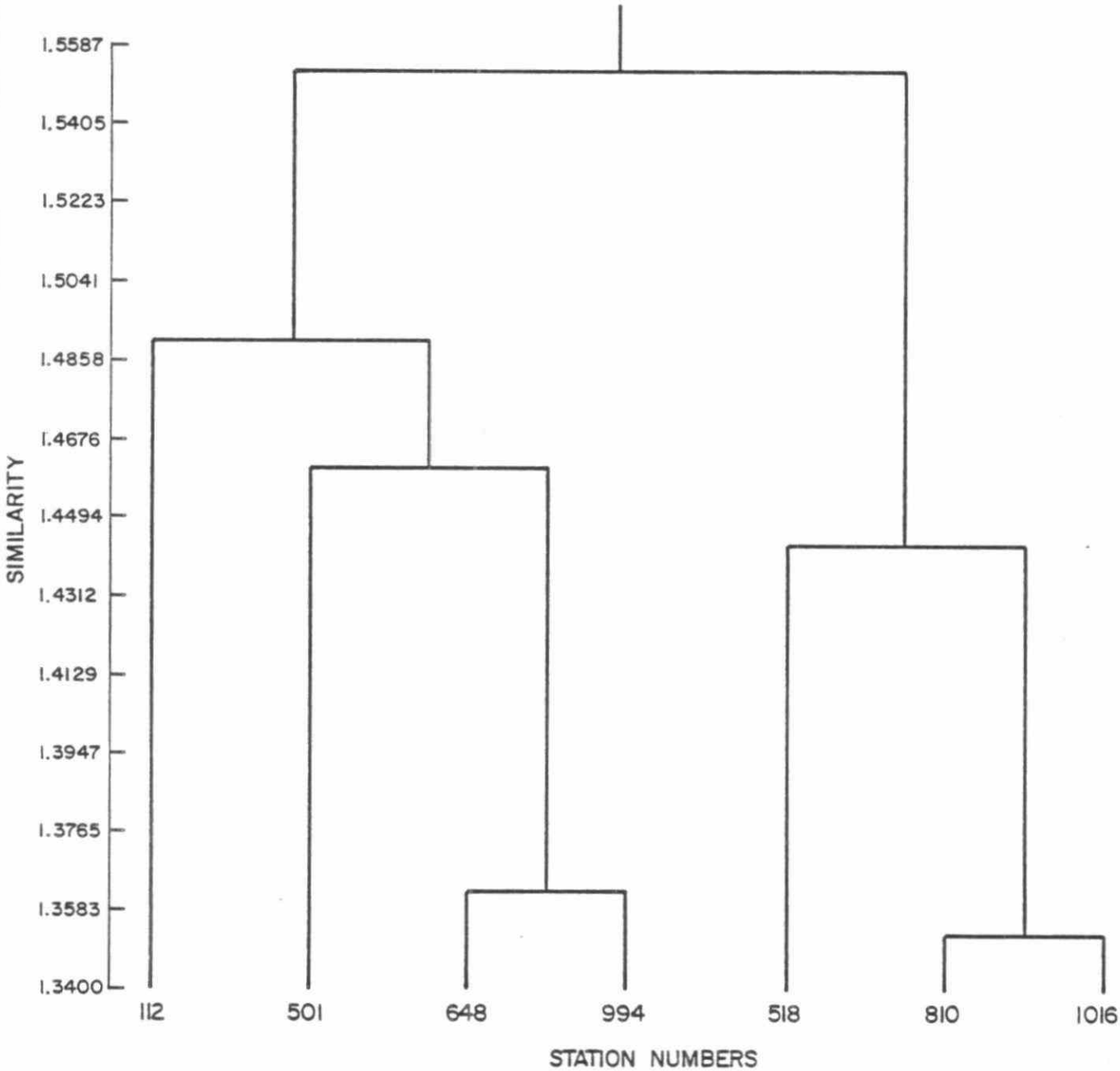


FIG. 4

MINISTRY OF THE ENVIRONMENT
NANTICOKE WATER QUALITY

DENDROGRAMS FOR 1969-1978 DATA

ACRES

water sampling stations can be clustered into a group of offshore stations and a group of other stations nearer shore.

Table 9 shows the two stations that cluster most closely for each one of 24 parameters in the second (1981 to 1983) data set. The pair of stations that clustered most closely for the greatest number of parameters (8) was 501 and 1086. These are the two stations farthest offshore.

It is surprising that Stations 1085 and 1087 do not cluster most closely for more parameters than they do (2). These two stations are nearer each other than to any other station and they are the stations nearest shore and nearest the mouth of Centre Creek. It may be that the Centre Creek mixing zone affects water quality differently at these two stations. This conjecture is strengthened by the relatively large number of parameters (5) for which 1087 clusters most closely with 1086. Water quality at Station 1087 seems to be more closely related to that at the stations in deeper water, 501 and 1086, than to that at its nearest neighbor, Station 1085.

Cluster analysis of the standardized, combined, 1981 to 1983 data, however, gives the three stations nearest the mouth of Centre Creek as one cluster and the offshore and control stations as another (Figure 5). Note, though, that Station 1085 is still less similar to 1086 and 1087 than these two stations are to each other. The narrow range of the similarity value (1.3317 - 1.4282) indicates that all five stations are closely related.

TABLE 9

PARAMETERS FOR WHICH PAIRS OF STATIONS CLUSTER MOST CLOSELY, 1981 TO 1983

Station	994	1085	1086	1087
501	turbidity	Cr	sp. cond.	
		Cu	NO_2 + NO_3	
			TKN	
			Kjel. org. N.	
			chlor. b	
			total P	
			Cd	
			Pb	
994			NO_3	temperature
			Ni	NH_3
			Fe	
			Ni	
1085				Secchi depth
				chlor. a
1086				Dis. Oxygen
				pH
				total N
				silicate
				Zn

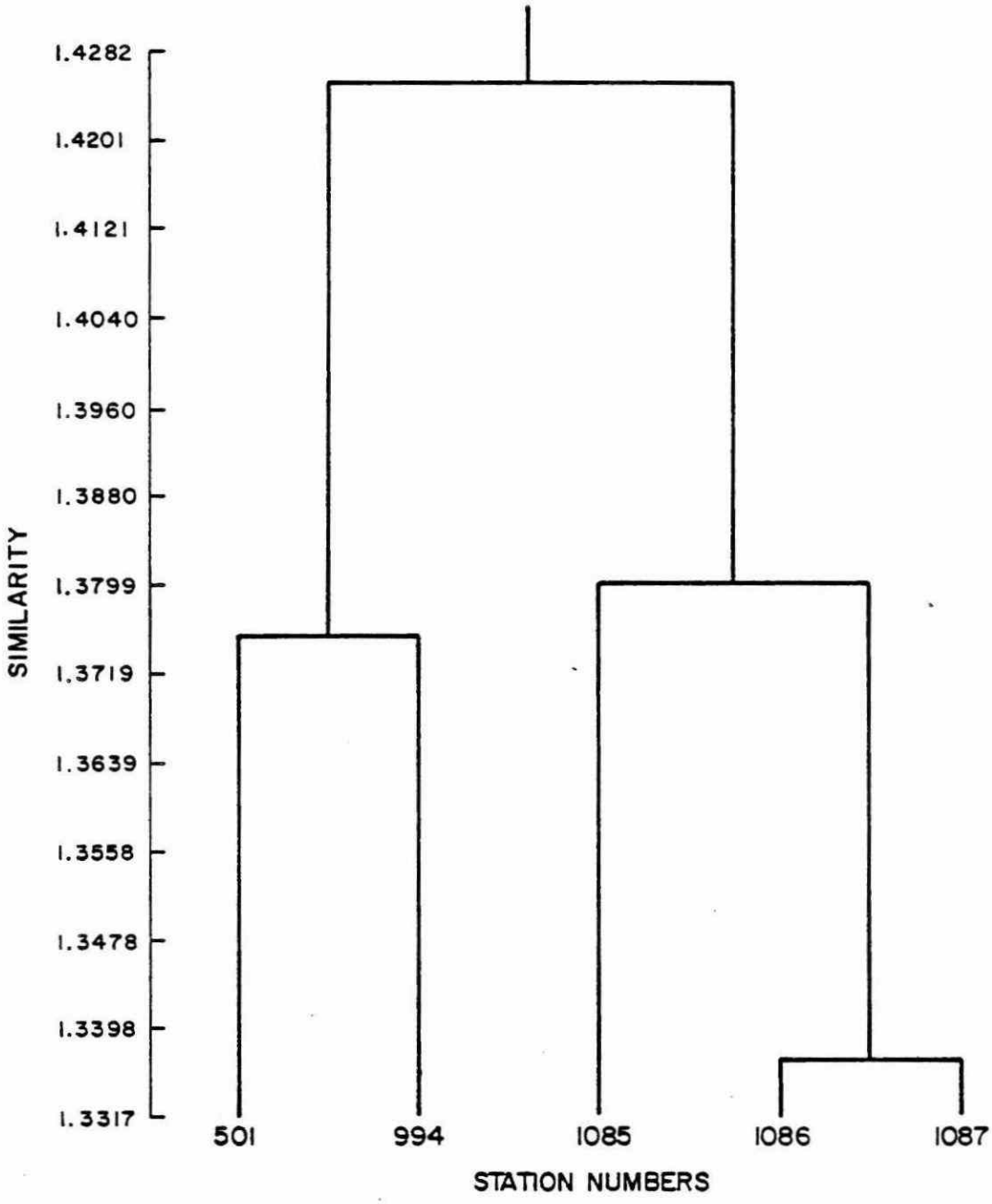


FIG. 5

MINISTRY OF THE ENVIRONMENT
NANTICOKE WATER QUALITY

DENDROGRAMS FOR 1981-1983 DATA

ACRES

3.3 - PWQO Exceedance

Nanticoke water quality data for four stations were compared with the MOE (1984) PWQO for the protection of aquatic life in surface waters. Table 10 shows the number of valid measurements for each of the four stations in each year of monitoring. Figures 6 to 17 show the percentage of samples exceeding the PWQO in each year and the average exceedance factors.

In the years that pH was measured, the PWQO was exceeded from time to time at each station. In general, exceeding pH values were higher than the upper limit of the PWQO. Only in a few instances was the exceeding pH lower than the lower limit of the PWQO. As a rule, fewer than 50% of the pH measurements exceeded the PWQO and average exceedance factors were nearly 1.

Percentage exceedance of the PWQO for phenols rose to a peak in the early 1970s and seems to have declined thereafter. Average exceedance factors also seemed to have declined during the monitoring period, with the conspicuous exception of the value for Station 501 in 1981.

Un-ionized ammonia values were calculated from total ammonia, field temperature, and field pH values. Accordingly, un-ionized ammonia exceedances were determined only for years in which field pH was measured: 1969-1970, 1978-1979, 1981-1983. In these years, exceedances were infrequent and small.

Neglecting Station 1085, total phosphorus exceedances also seem to have declined at Nanticoke. In the last 6 years of monitoring, percentage exceedance was always highest at Station 1085, which is the station nearest shore and nearest the mouth of a tributary. During these years, average

TABLE 10

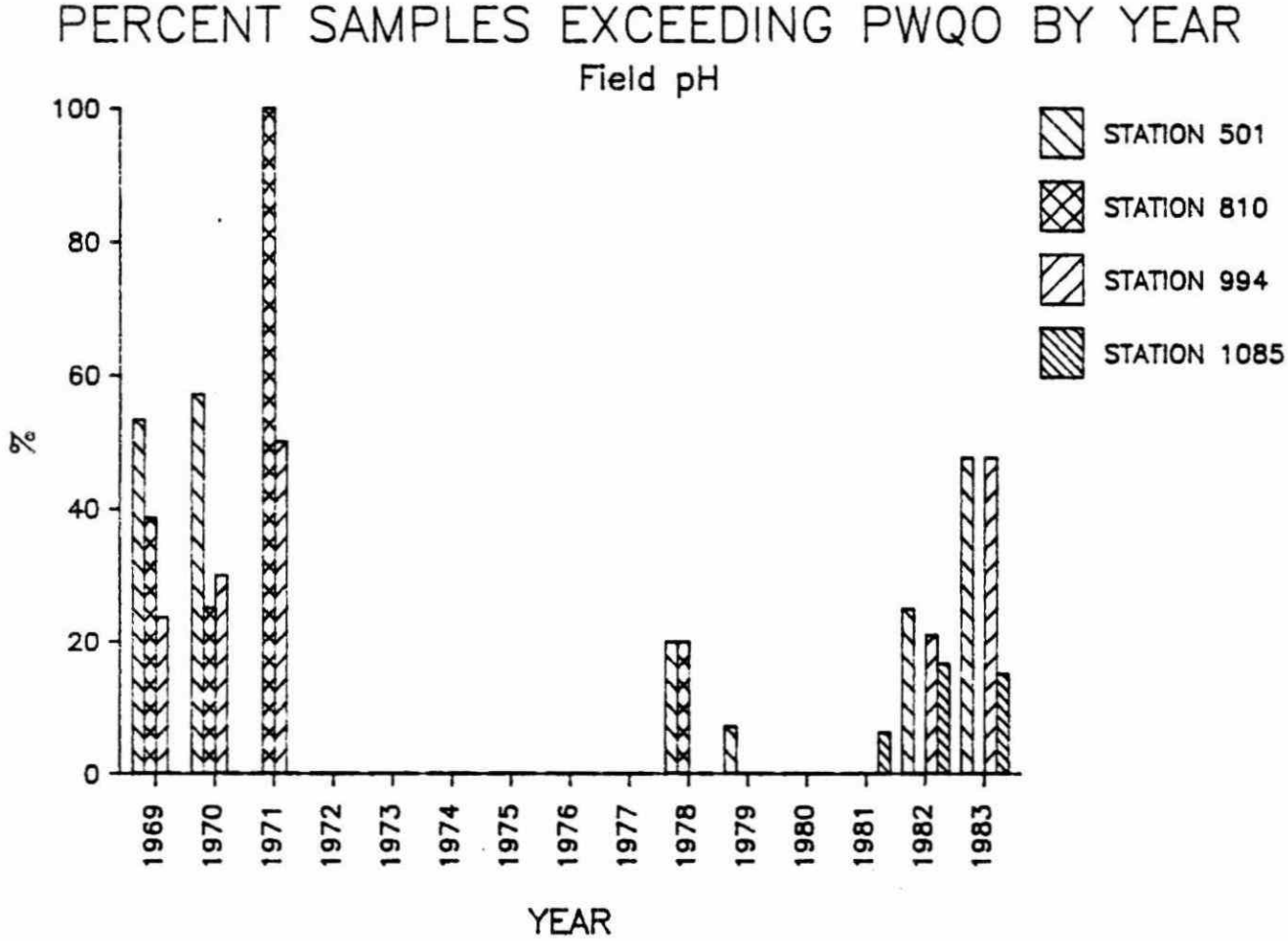
NUMBERS OF VALID MEASUREMENTS COMPARED WITH PWQO

Parameter	PWQO	Number of Valid* Measurements for Each of Four Stations** by Year***																													
		1969		1970		1971		1972		1973		1974		1975		1976		1977		1978		1979		1980		1981		1982		1983	
pH field	6.5 - 8.5	15	13	7	8	0	1	0	0	0	0	0	0	0	0	0	0	0	0	15	15	14	14	-	0	27	-	32	-	42	-
		17		10		2		0		0		0		0		0		0		0	0	-	14	0	0	15	16	19	18	21	20
pH lab	6.5 - 8.5	0	0	0	0	7	7	7	7	8	12	20	19	16	16	16	16	11	12	3	3	0	0	-	0	24	-	0	-	0	-
		0		0		7		7		11		18		16		16		12		3	3	-	0	23	13	12	12	0	0	0	0
Phenolics	1 µg/L	15	13	3	5	5	5	8	8	9	11	18	17	14	14	16	16	12	12	16	18	9	9	-	0	36	-	0	-	0	-
		17		6		7		8		10		17		14		16		12		10	3	-	10	33	18	18	17	0	0	0	0
Ammonia, un-ionized	0.02 mg/L	13	11	7	8	0	1	0	0	0	0	0	0	0	0	0	0	0	0	15	15	14	14	-	0	25	-	28	-	40	-
		16		10		2		0		0		0		0		0		0		0	0	-	14	0	0	14	14	16	16	20	20
Phosphorus, total	0.020 mg/L	15	13	7	8	8	8	9	7	12	14	18	18	16	16	43	34	26	25	43	40	30	21	-	0	37	-	30	-	40	-
		17		10		10		8		14		18		16		34		26		21	11	-	18	33	18	18	18	18	17	20	20
Cadmium	0.0002 mg/L	0	0	0	0	0	0	0	0	1	1	0	0	0	0	0	0	0	0	10	16	6	6	-	0	35	-	27	-	28	-
		0		0		0		0		1		0		0		0		0		10	5	-	6	8	3	18	18	16	14	14	14
Chromium	0.1 mg/L	0	0	0	0	0	0	2	2	1	1	0	0	0	0	0	0	0	0	10	16	6	6	-	0	36	-	27	-	42	-
		0		0		0		2		1		0		0		0		0		10	5	-	6	29	16	18	18	16	14	21	20
Copper	0.005 mg/L	0	0	0	0	0	0	0	0	1	0	0	0	5	2	0	0	0	0	2	4	1	2	-	0	36	-	27	-	42	-
		0		0		0		0		0		0		4		0		0		3	2	-	3	21	11	18	18	16	13	21	20
Iron	0.300 mg/L	0	0	0	0	0	0	2	2	10	11	18	16	14	14	16	16	12	12	19	20	23	19	-	0	37	-	31	-	40	-
		0		0		0		2		11		18		13		16		12		10	5	-	16	29	16	18	18	18	18	20	20
Nickel	0.025 mg/L	0	0	0	0	0	0	0	0	0	0	0	0	14	12	0	0	0	0	10	13	6	6	-	0	36	-	27	-	42	-
		0		0		0		0		0		0		14		0		0		10	5	-	6	29	16	18	18	16	14	21	20
Lead	0.025 mg/L	0	0	0	0	0	0	0	0	1	1	0	0	14	12	0	0	0	0	0	0	1	0	-	0	36	-	27	-	42	-
		0		0		0		0		1		0		14		0		0		0	0	-	0	10	5	18	18	16	14	21	20
Zinc	0.030 mg/L	0	0	0	0	0	0	2	2	0	1	0	0	14	12	0	0	0	0	10	16	6	6	-	0	36	-	27	-	42	-
		0		0		0		2		0		0		14		0		0		10	5	-	6	29	16	18	18	16	14	21	20

* A valid measurement is a reliably detected value or a value reported as a detection limit, if the detection limit is less than the PWQO.

** 501 | 810 - order of stations.
994 | 1085

***A blank space for a station in a given year means that the station had not yet been established.
A dash (-) means that the station had been established, but was not sampled in that year.


PERCENT SAMPLES EXCEEDING PWQO BY YEAR
Field pH
100
80
60
40
20
0
%
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983
YEAR
STATION 501
STATION 810
STATION 994
STATION 1085

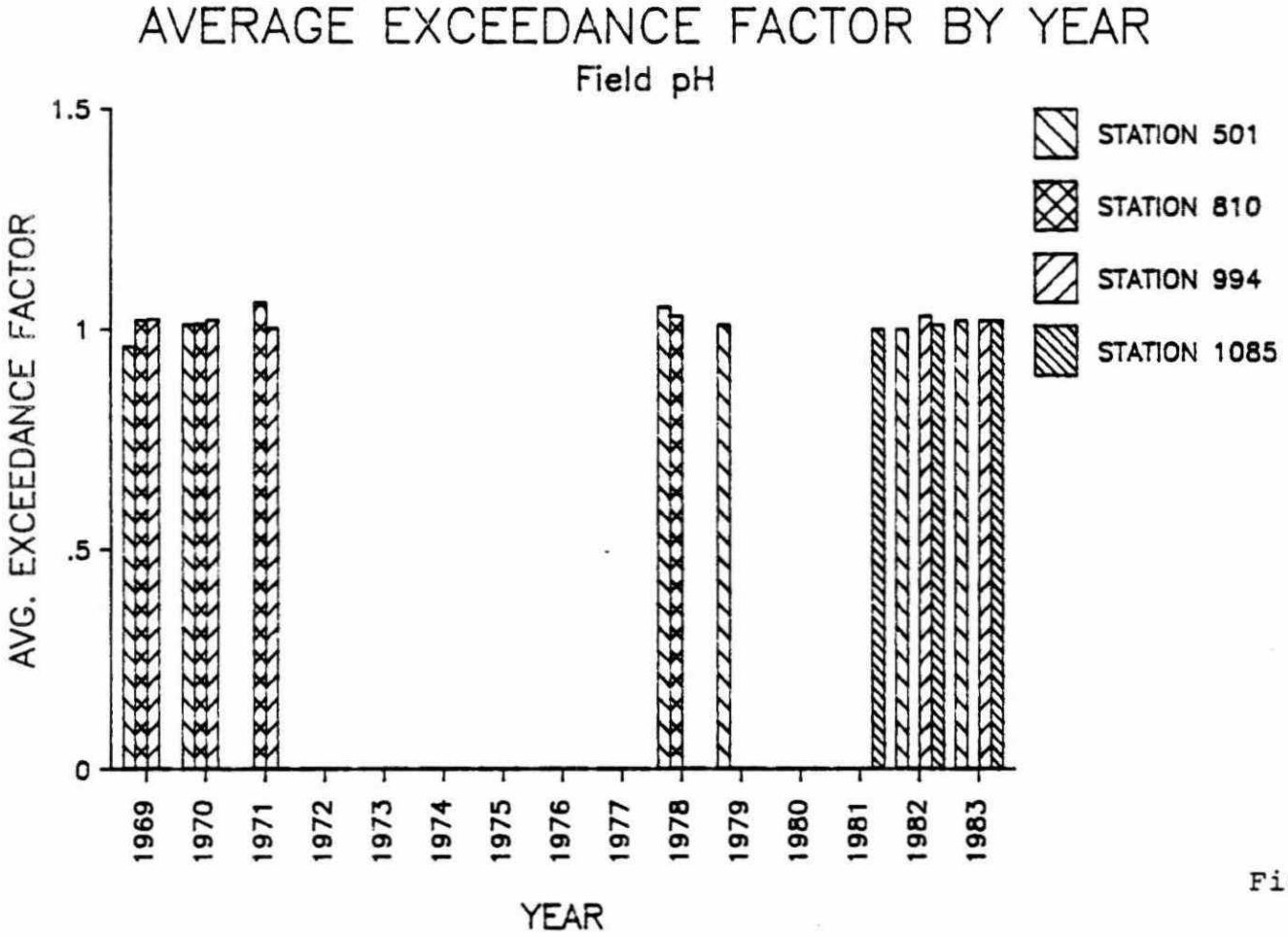
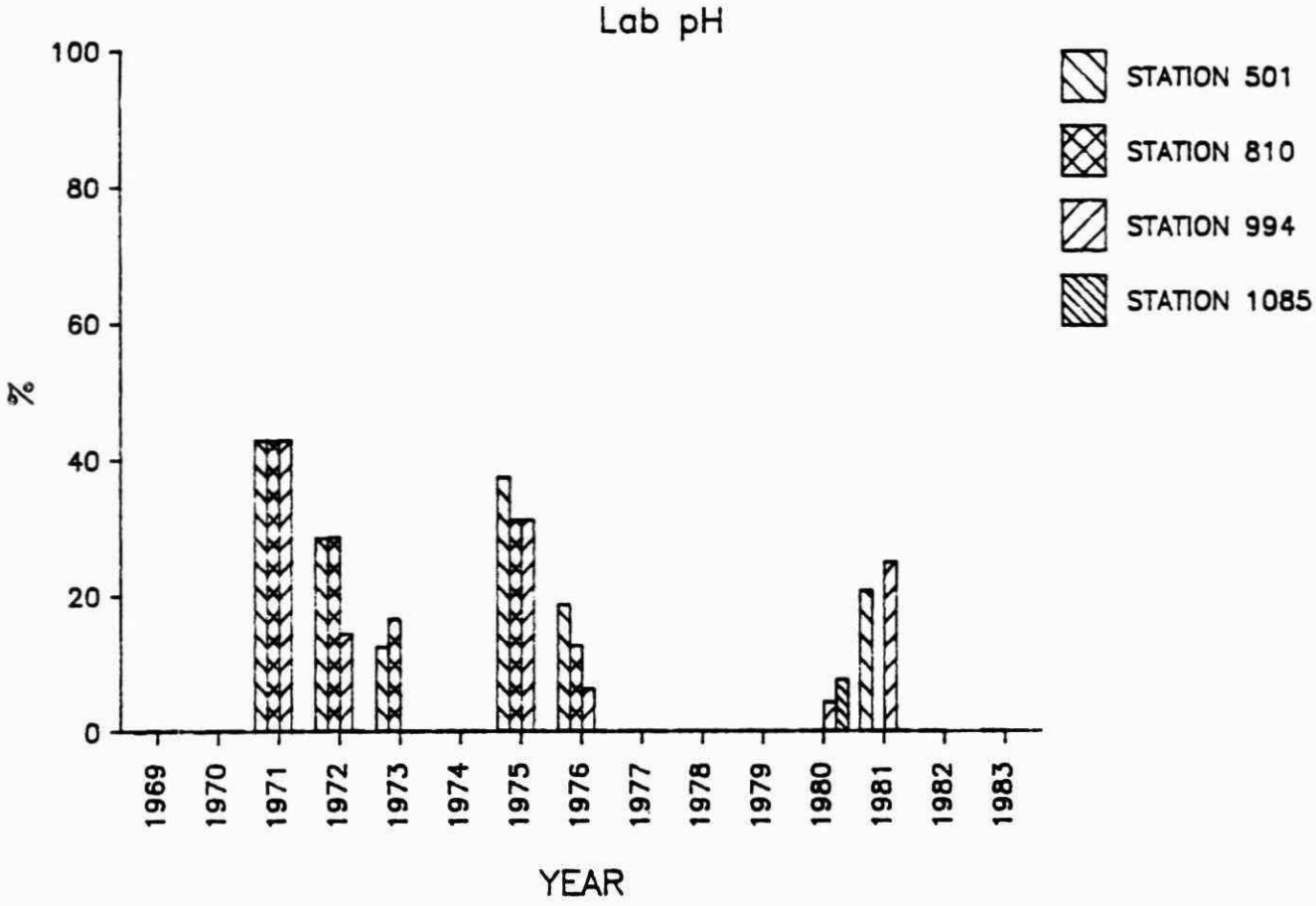

AVERAGE EXCEEDANCE FACTOR BY YEAR
Field pH
1.5
1
.5
0
AVG. EXCEEDANCE FACTOR
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983
YEAR
STATION 501
STATION 810
STATION 994
STATION 1085

Fig. 6


PERCENT SAMPLES EXCEEDING PWQO BY YEAR
Lab pH
100
80
60
40
20
0
%
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983
YEAR
STATION 501
STATION 810
STATION 994
STATION 1085

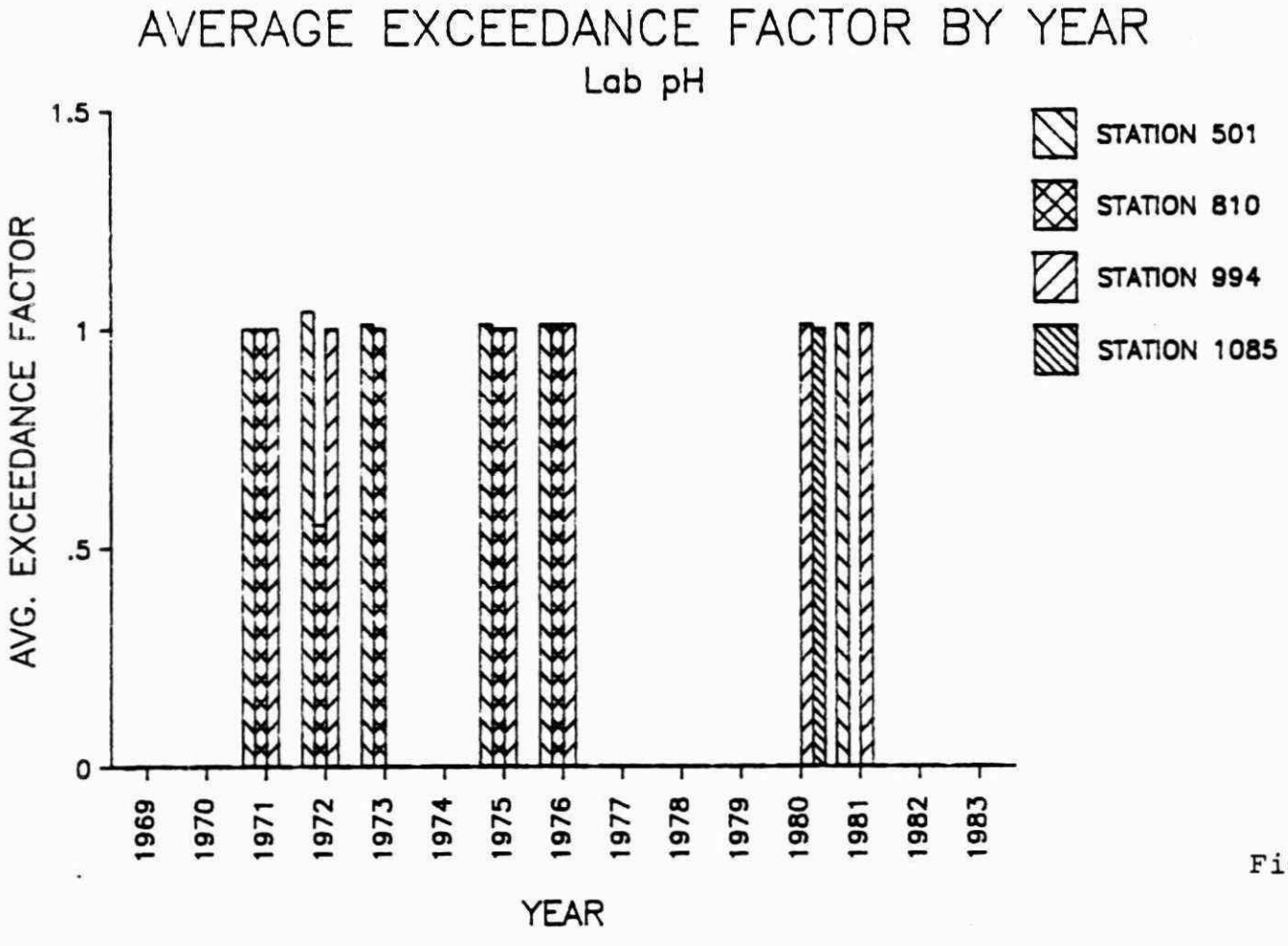
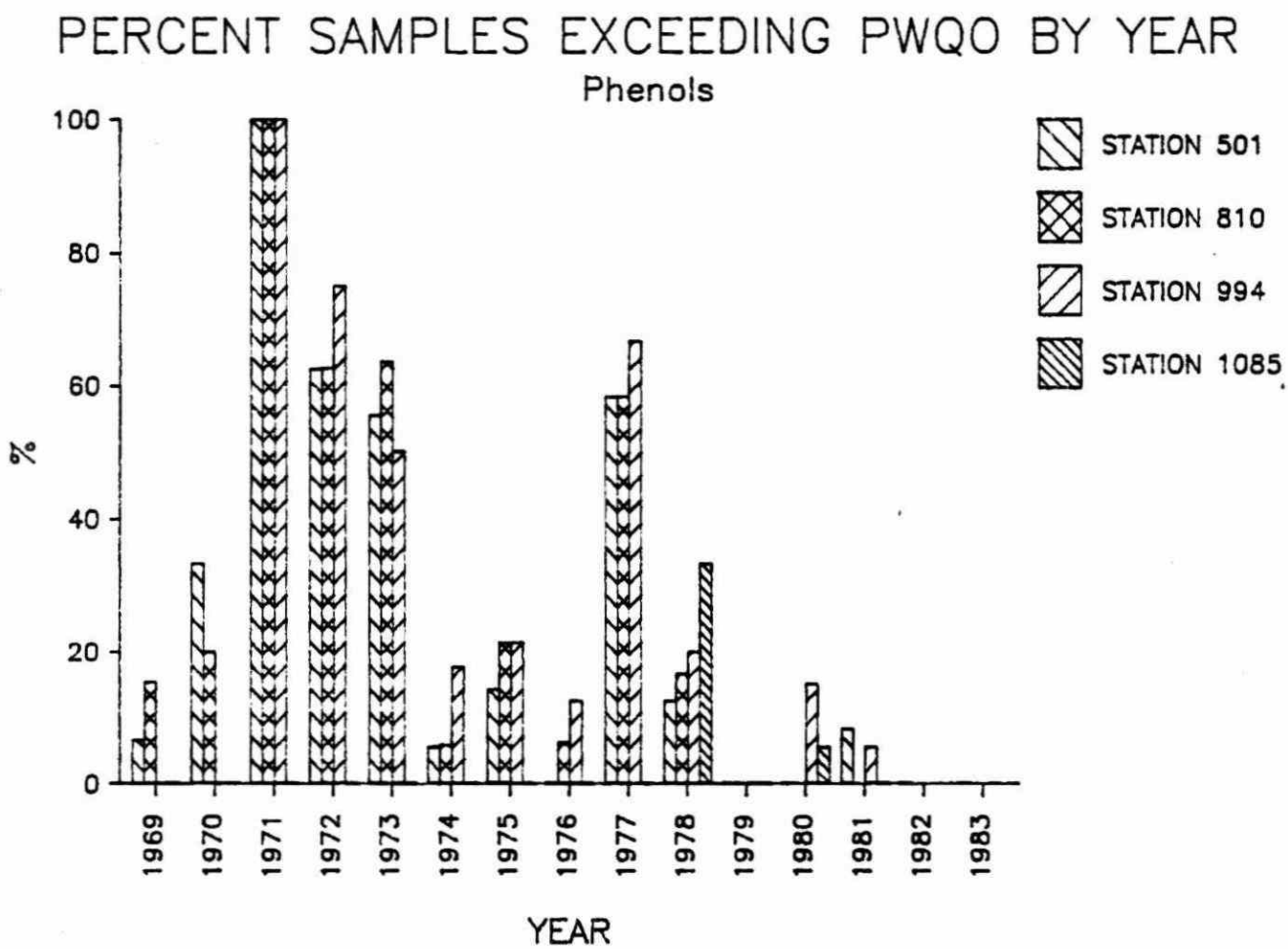

AVERAGE EXCEEDANCE FACTOR BY YEAR
Lab pH
1.5
1
.5
0
AVG. EXCEEDANCE FACTOR
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983
YEAR
STATION 501
STATION 810
STATION 994
STATION 1085

Fig. 7


PERCENT SAMPLES EXCEEDING PWQO BY YEAR
Phenols
100
80
60
40
20
0
%
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983
YEAR
STATION 501
STATION 810
STATION 994
STATION 1085

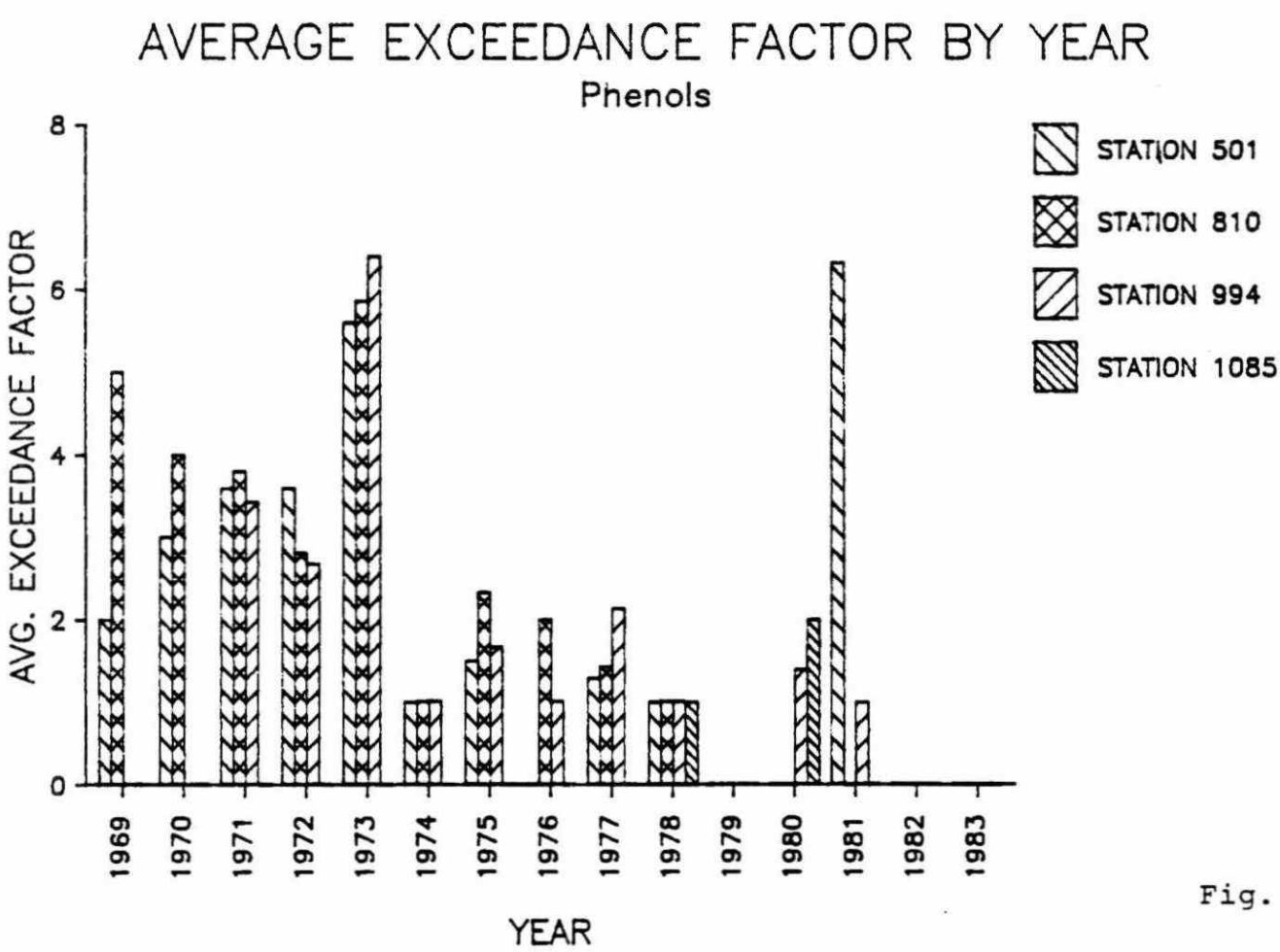
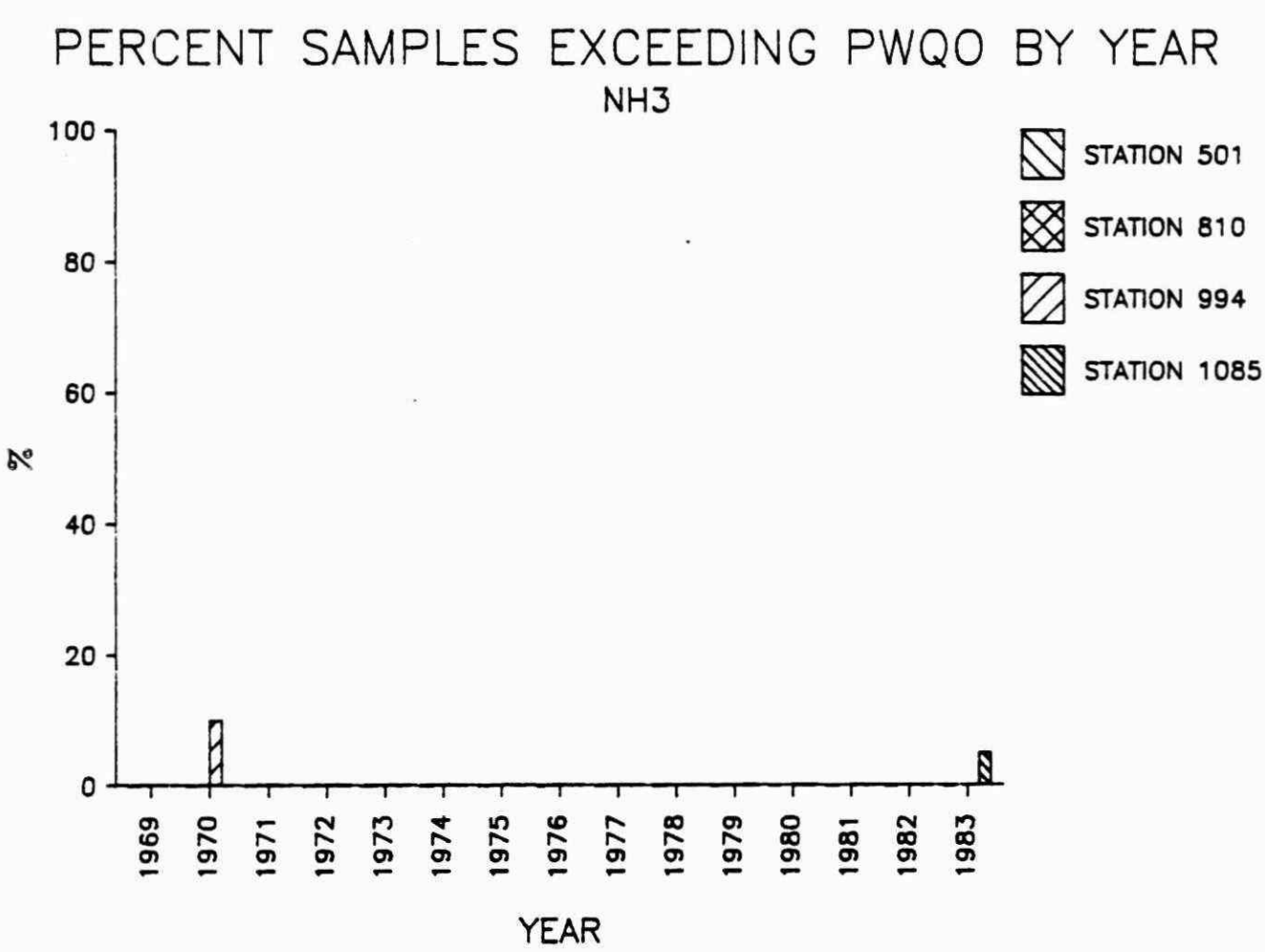

AVERAGE EXCEEDANCE FACTOR BY YEAR
Phenols
8
6
4
2
0
AVG. EXCEEDANCE FACTOR
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983
YEAR
STATION 501
STATION 810
STATION 994
STATION 1085

Fig. 8


PERCENT SAMPLES EXCEEDING PWQO BY YEAR
NH3
100
80
60
40
20
0
%
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983
YEAR
STATION 501
STATION 810
STATION 994
STATION 1085

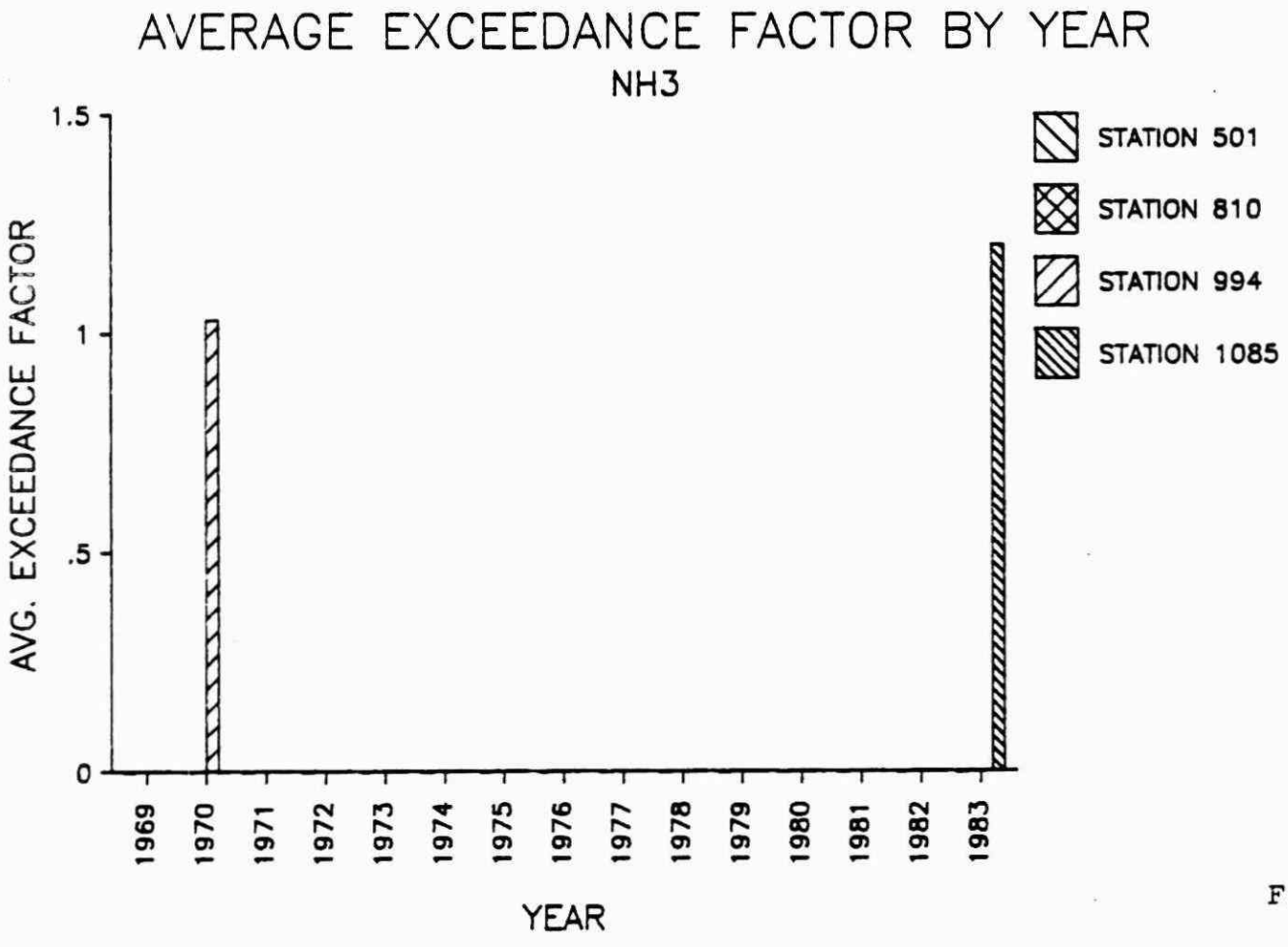
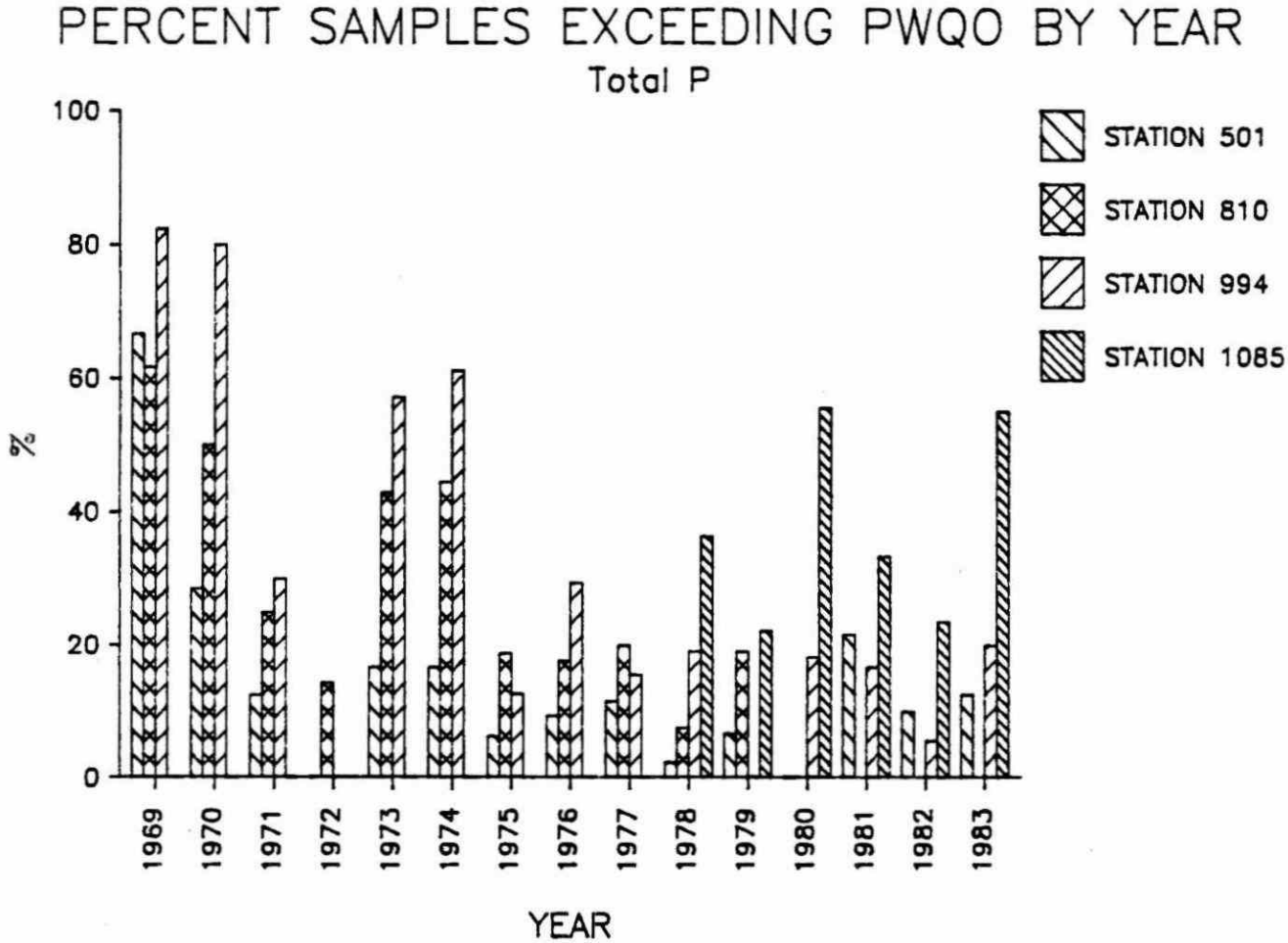

AVERAGE EXCEEDANCE FACTOR BY YEAR
NH3
1.5
1
.5
0
AVG. EXCEEDANCE FACTOR
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983
YEAR
STATION 501
STATION 810
STATION 994
STATION 1085

Fig. 9


PERCENT SAMPLES EXCEEDING PWQO BY YEAR
Total P
100
80
60
40
20
0
%
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983
YEAR
STATION 501
STATION 810
STATION 994
STATION 1085

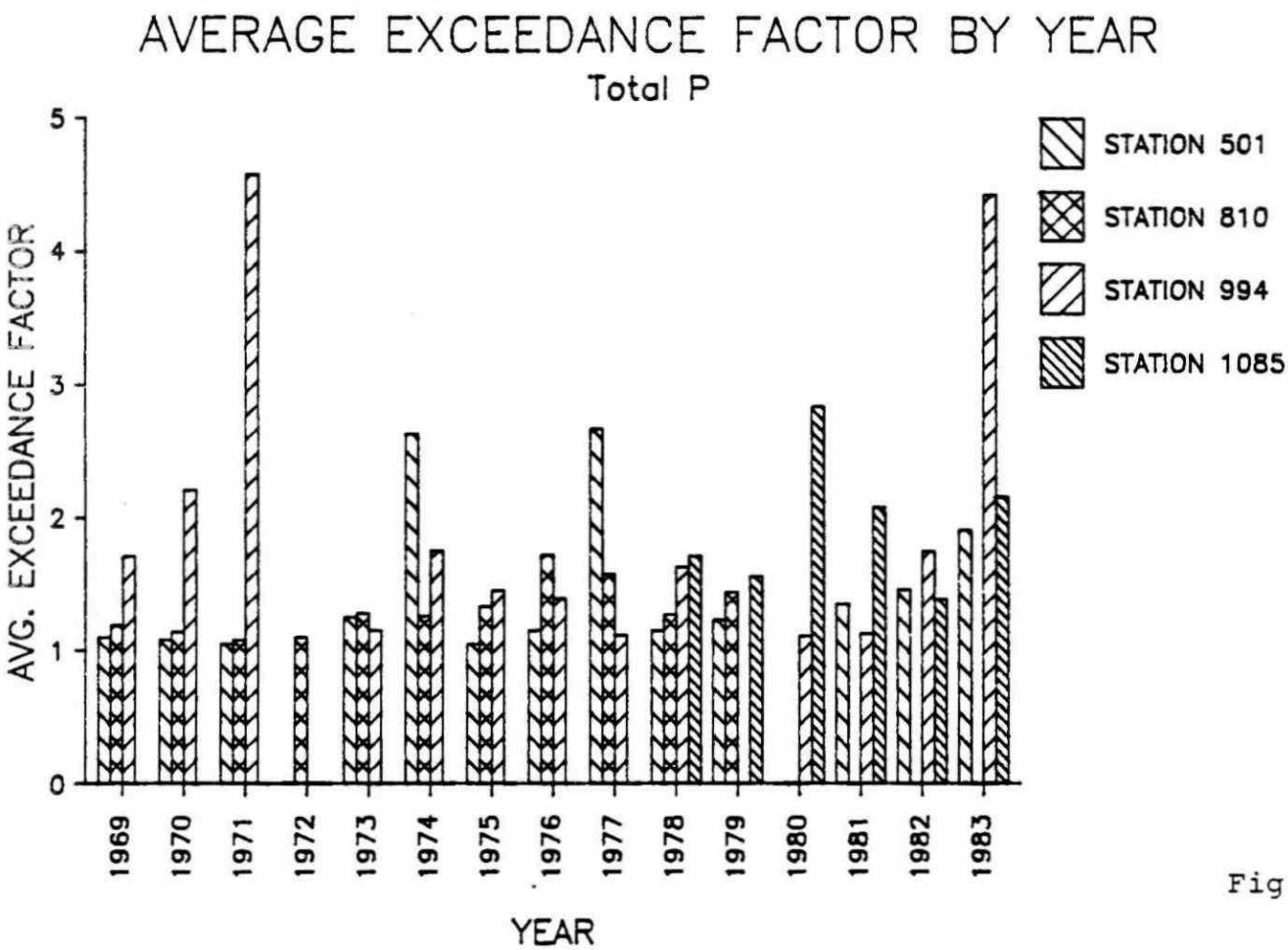
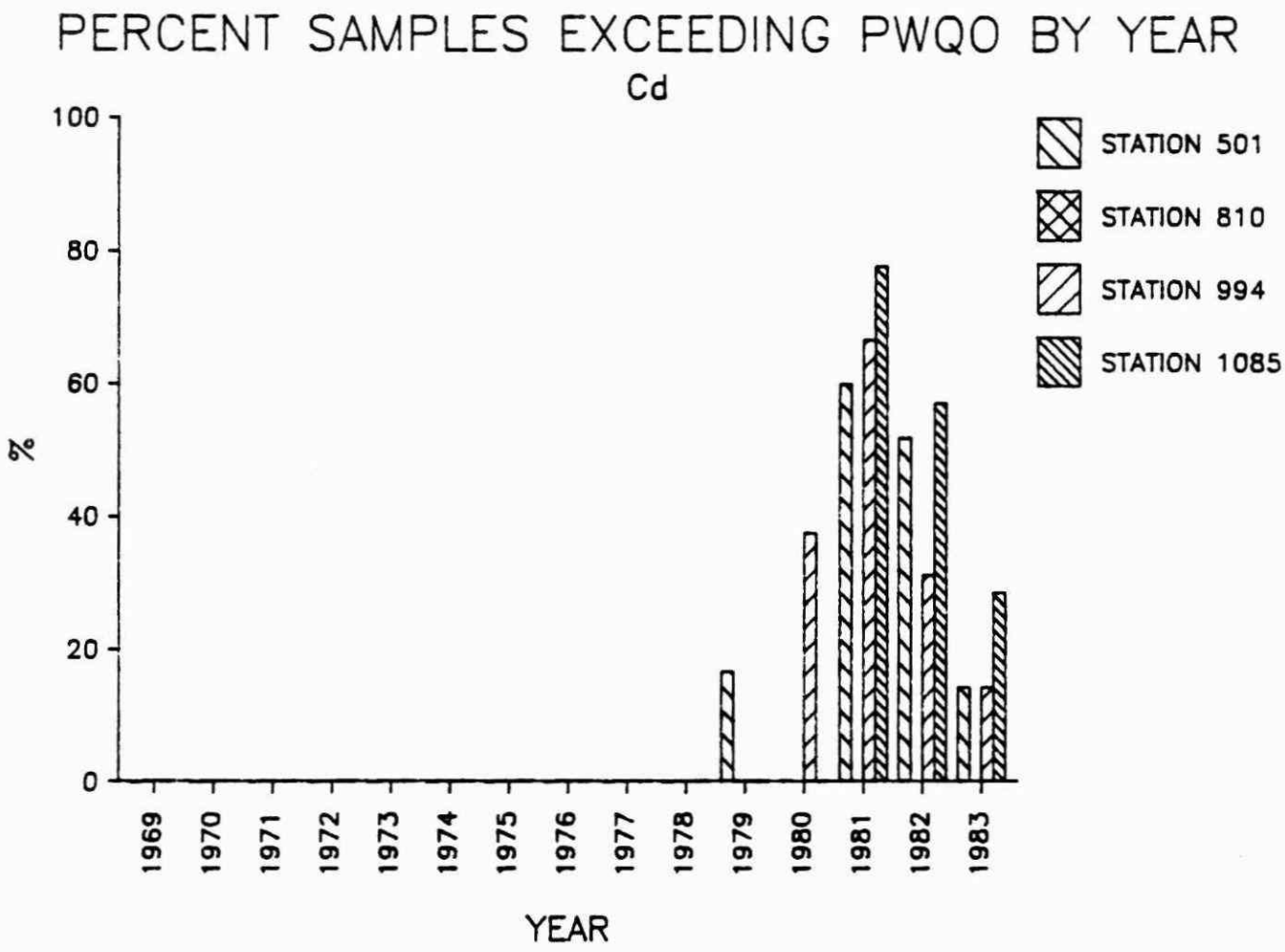

AVERAGE EXCEEDANCE FACTOR BY YEAR
Total P
5
4
3
2
1
0
AVG. EXCEEDANCE FACTOR
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983
YEAR
STATION 501
STATION 810
STATION 994
STATION 1085

Fig. 10


PERCENT SAMPLES EXCEEDING PWQO BY YEAR
Cd
100
80
60
40
20
0
%
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983
YEAR
STATION 501
STATION 810
STATION 994
STATION 1085

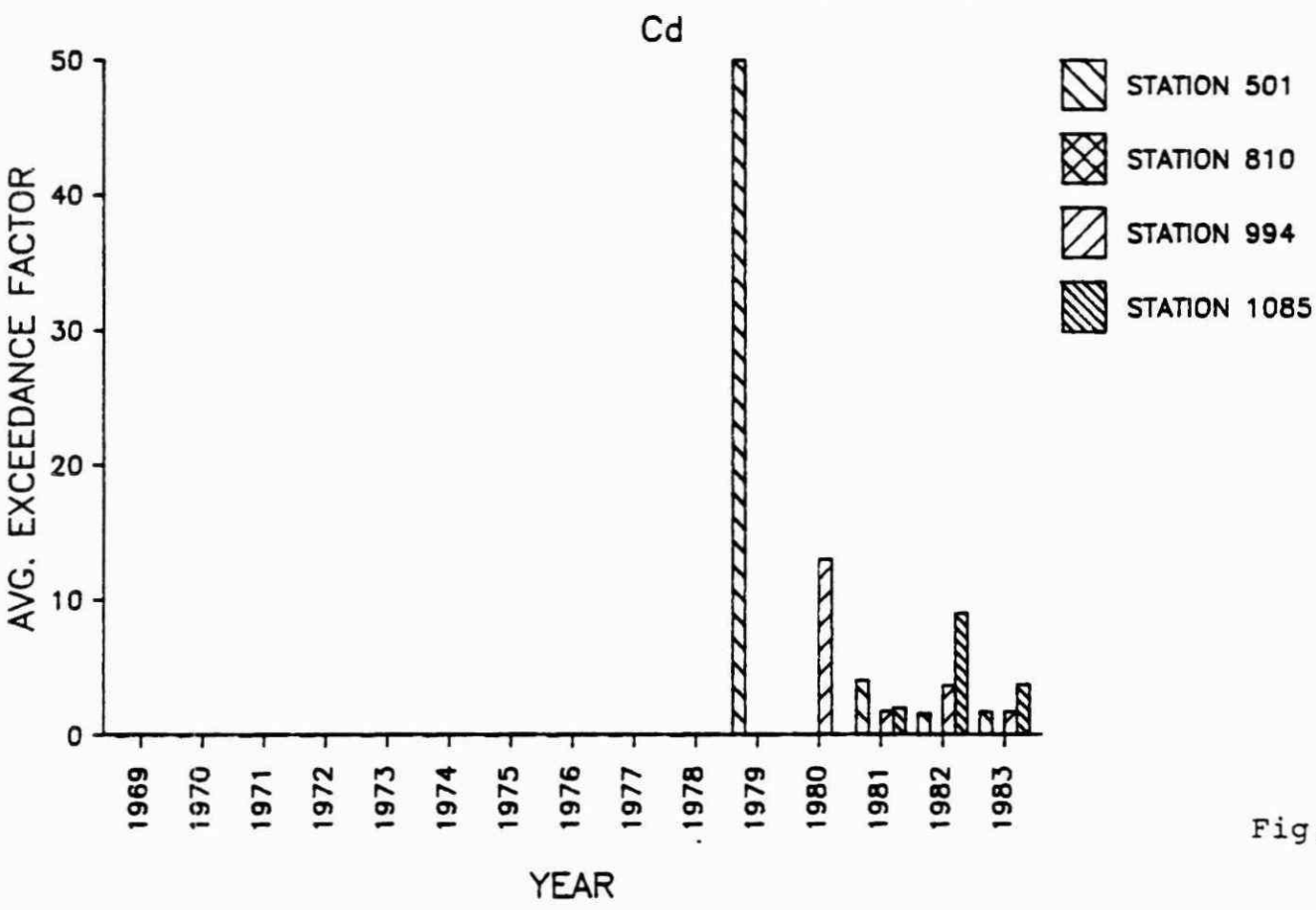
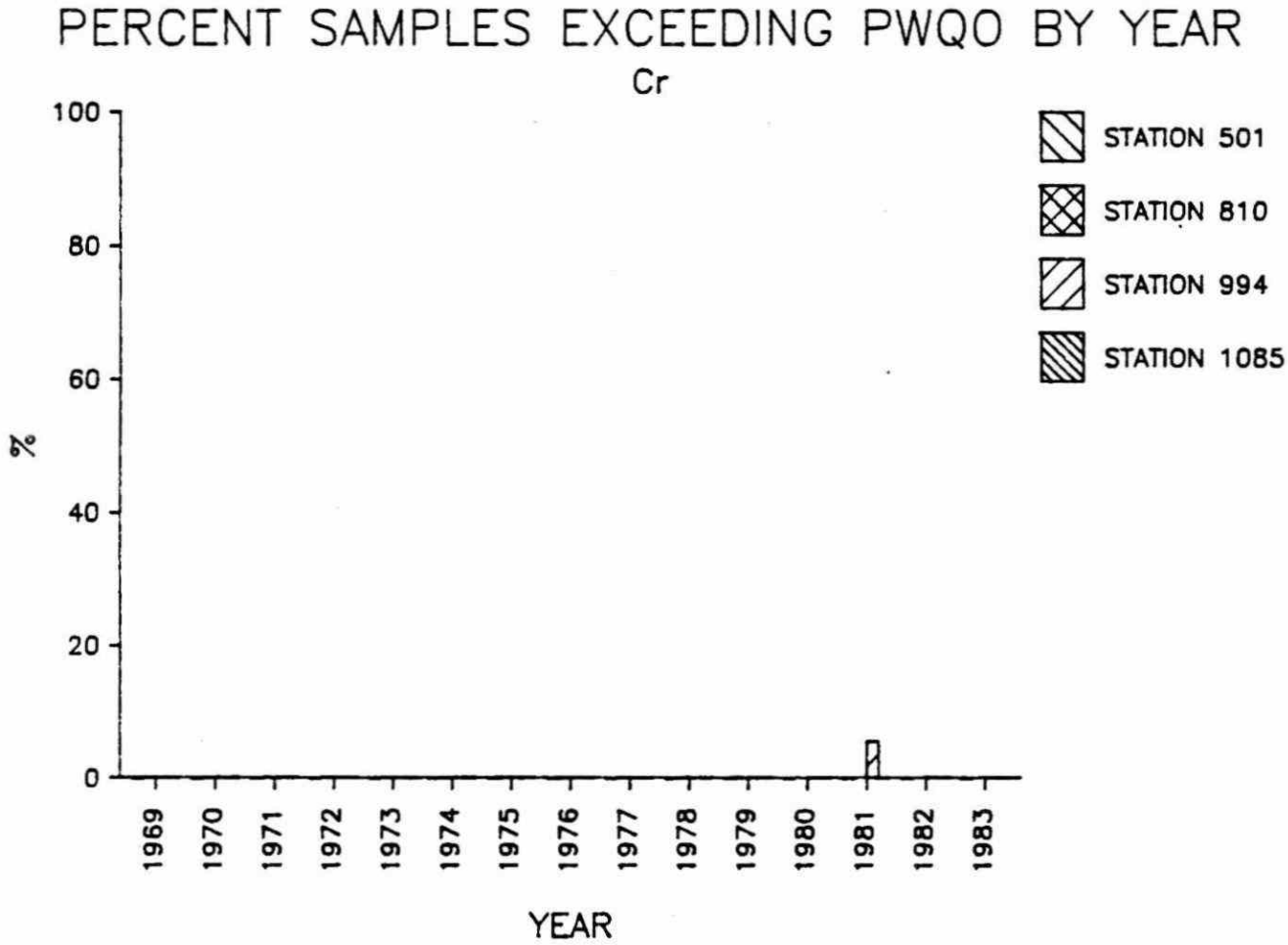

AVERAGE EXCEEDANCE FACTOR BY YEAR
Cd
50
40
30
20
10
0
AVG. EXCEEDANCE FACTOR
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983
YEAR
STATION 501
STATION 810
STATION 994
STATION 1085

Fig. 11


PERCENT SAMPLES EXCEEDING PWQO BY YEAR
Cr
100
80
60
40
20
0
%
STATION 501
STATION 810
STATION 994
STATION 1085
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983
YEAR

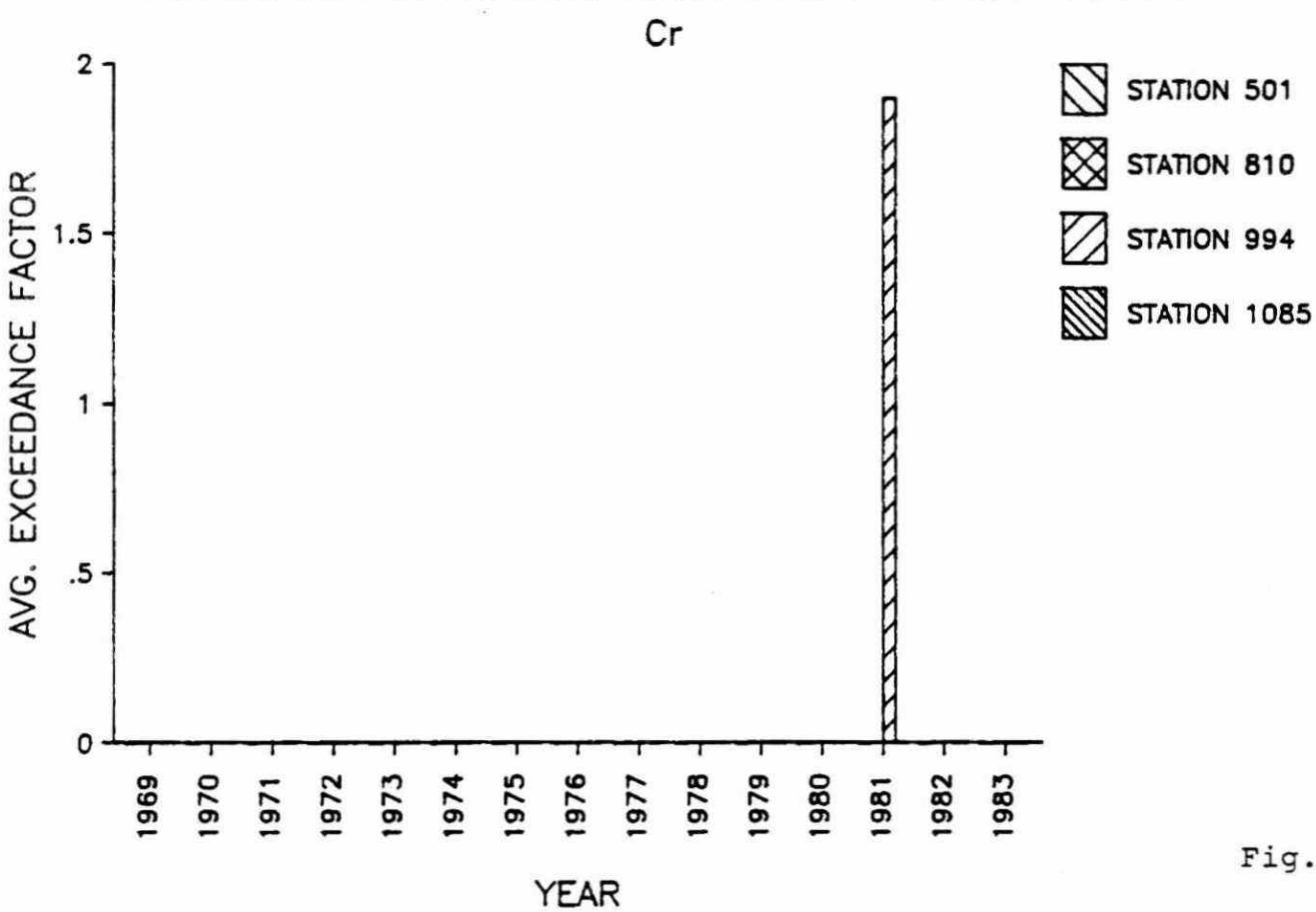
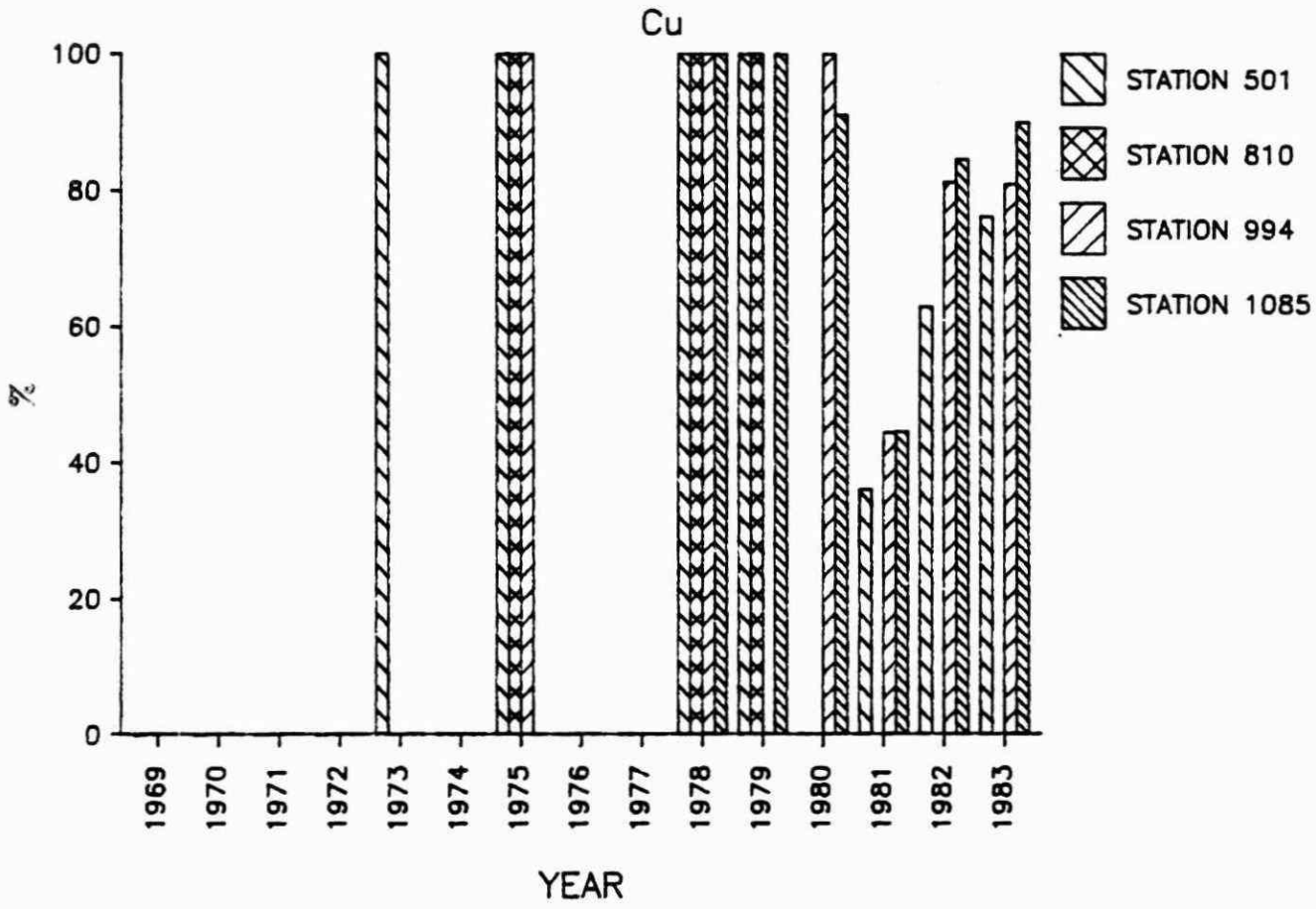

AVERAGE EXCEEDANCE FACTOR BY YEAR
Cr
2
1.5
1
.5
0
AVG. EXCEEDANCE FACTOR
STATION 501
STATION 810
STATION 994
STATION 1085
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983
YEAR

Fig. 12


PERCENT SAMPLES EXCEEDING PWQO BY YEAR
Cu
100
80
60
40
20
0
%
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983
YEAR
STATION 501
STATION 810
STATION 994
STATION 1085

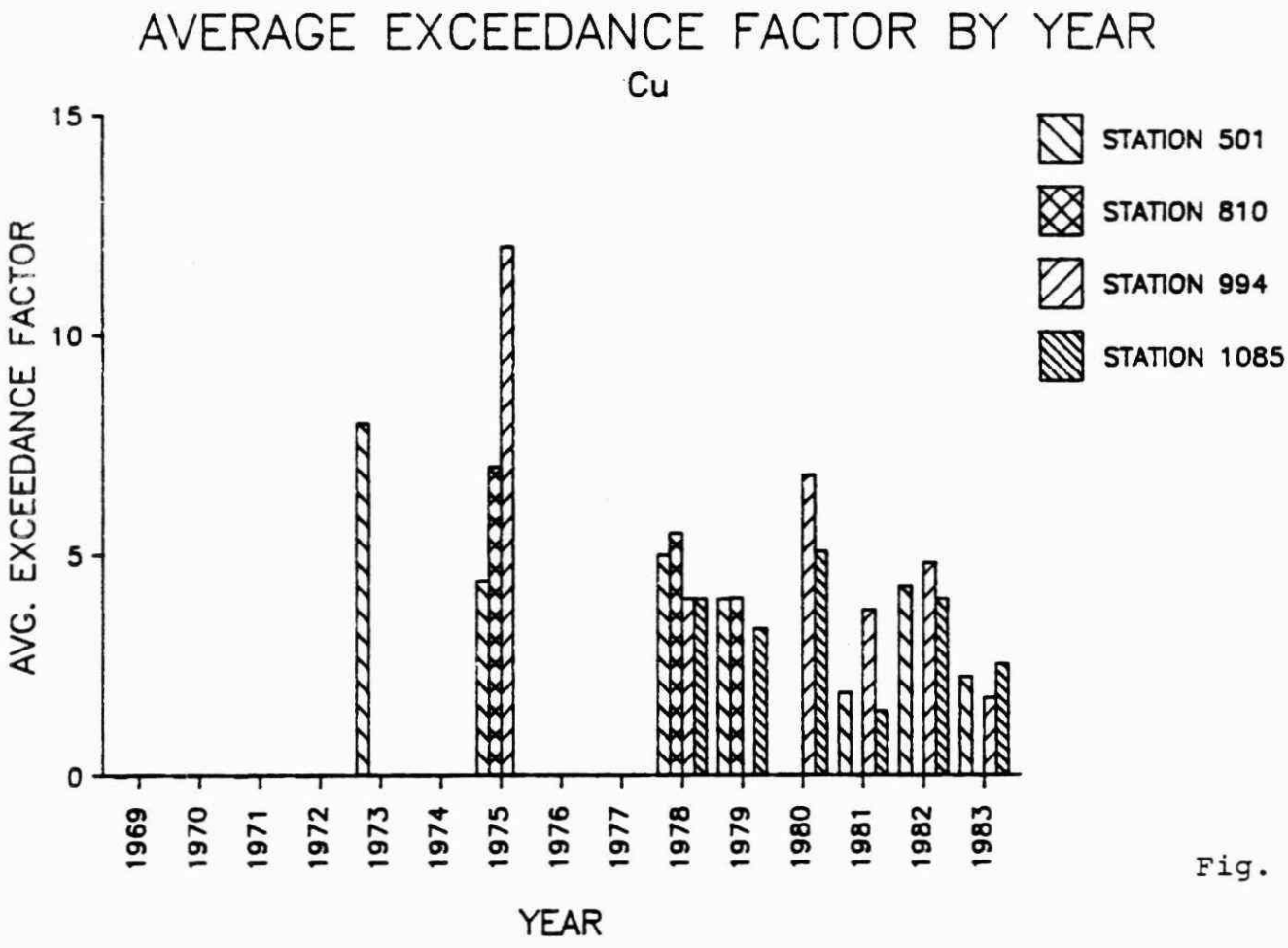
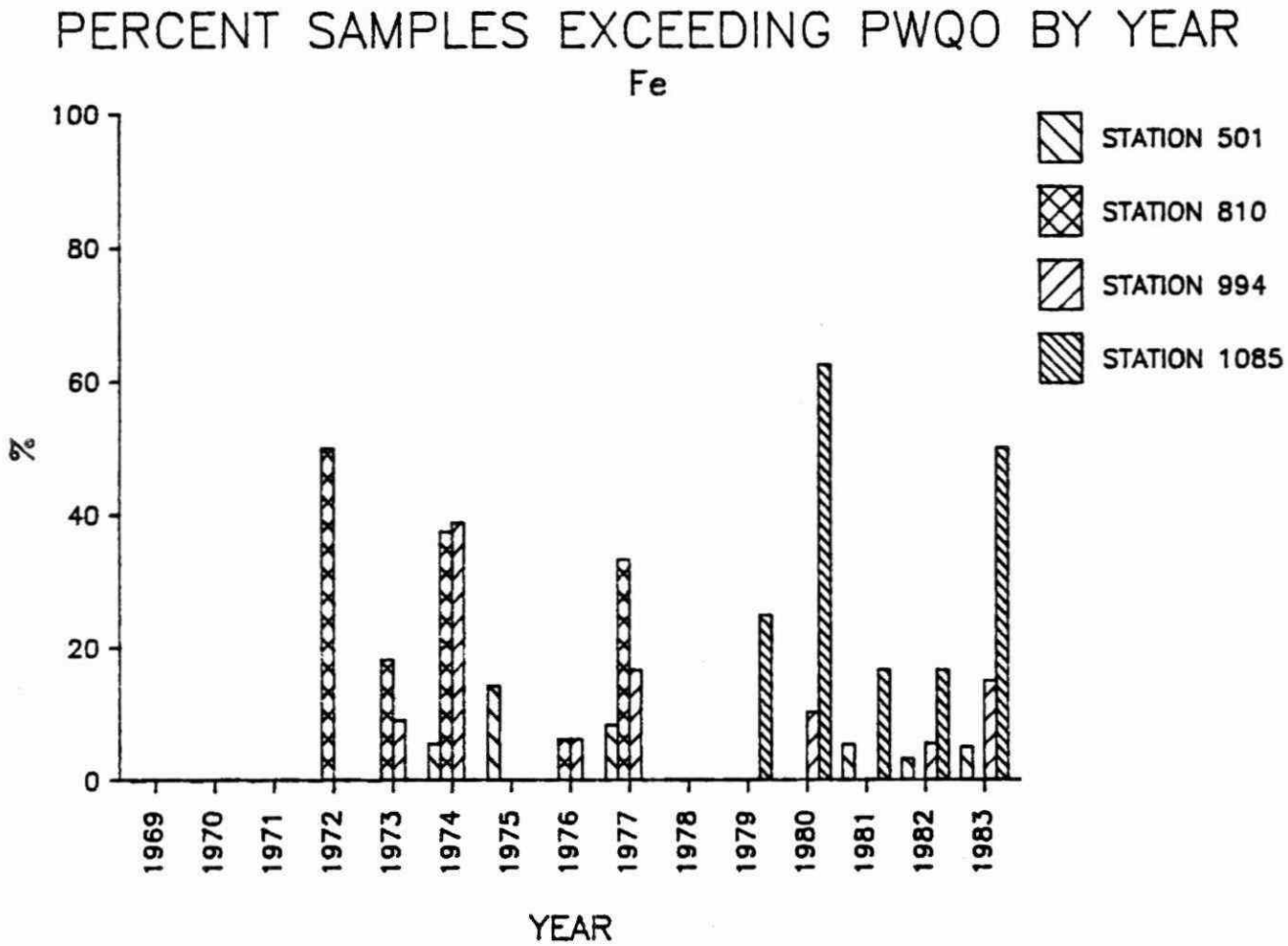

AVERAGE EXCEEDANCE FACTOR BY YEAR
Cu
15
10
5
0
AVG. EXCEEDANCE FACTOR
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983
YEAR
STATION 501
STATION 810
STATION 994
STATION 1085

Fig. 13


PERCENT SAMPLES EXCEEDING PWQO BY YEAR
Fe
100
80
60
40
20
0
%
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983
YEAR
STATION 501
STATION 810
STATION 994
STATION 1085

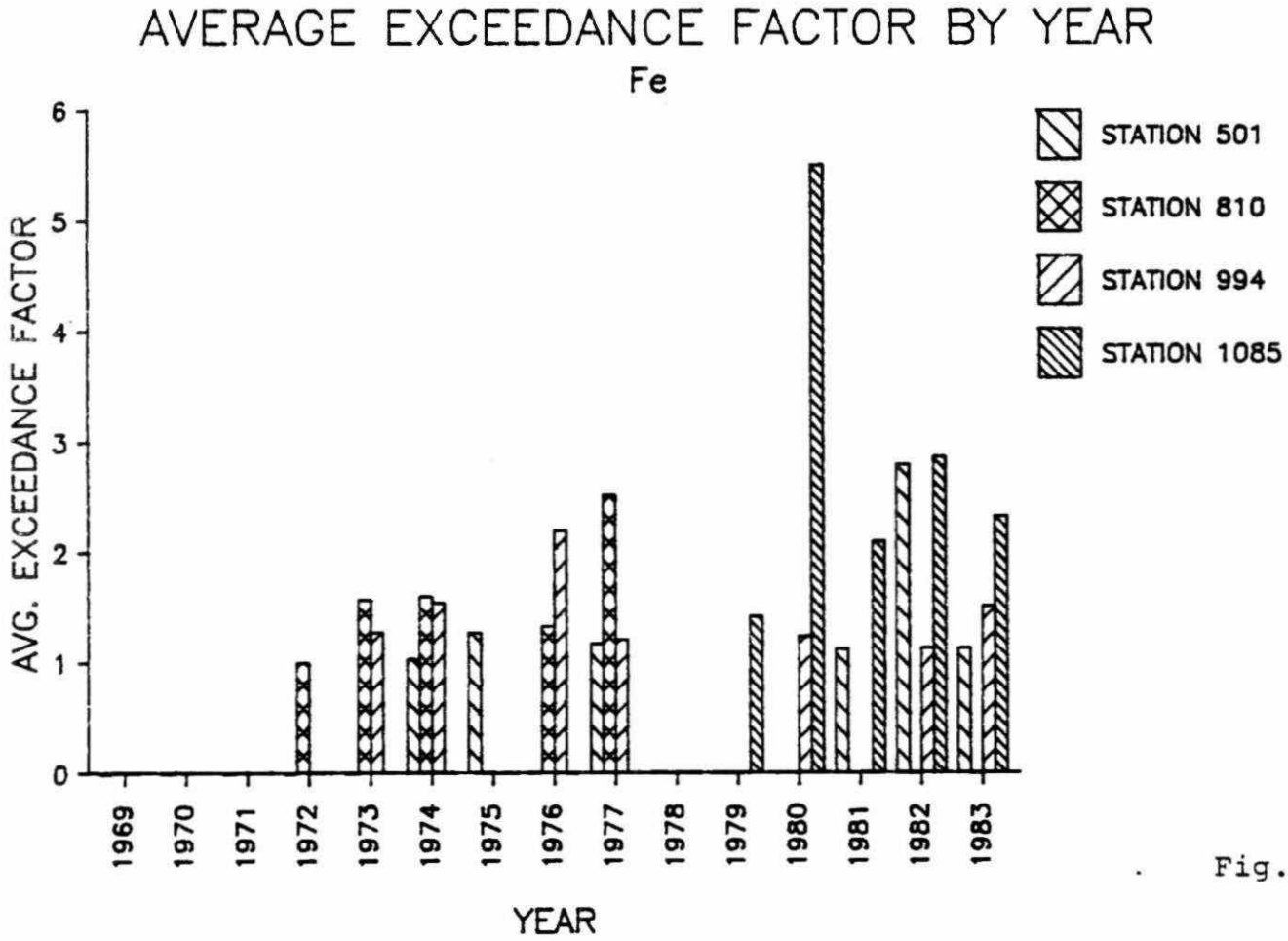
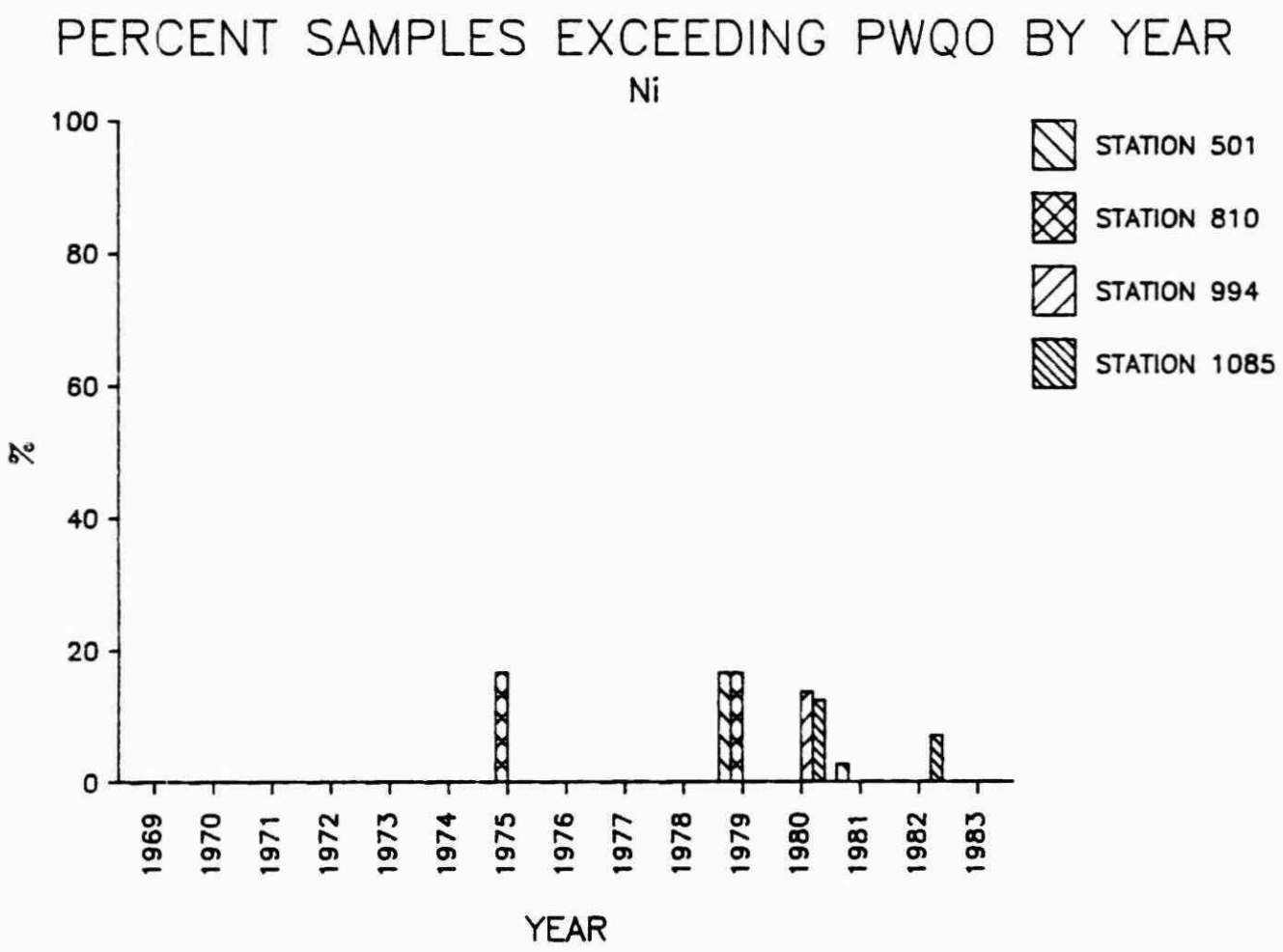

AVERAGE EXCEEDANCE FACTOR BY YEAR
Fe
6
5
4
3
2
1
0
AVG. EXCEEDANCE FACTOR
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983
YEAR
STATION 501
STATION 810
STATION 994
STATION 1085

Fig. 14


PERCENT SAMPLES EXCEEDING PWQO BY YEAR
Ni
100
80
60
40
20
0
%
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983
YEAR
STATION 501
STATION 810
STATION 994
STATION 1085

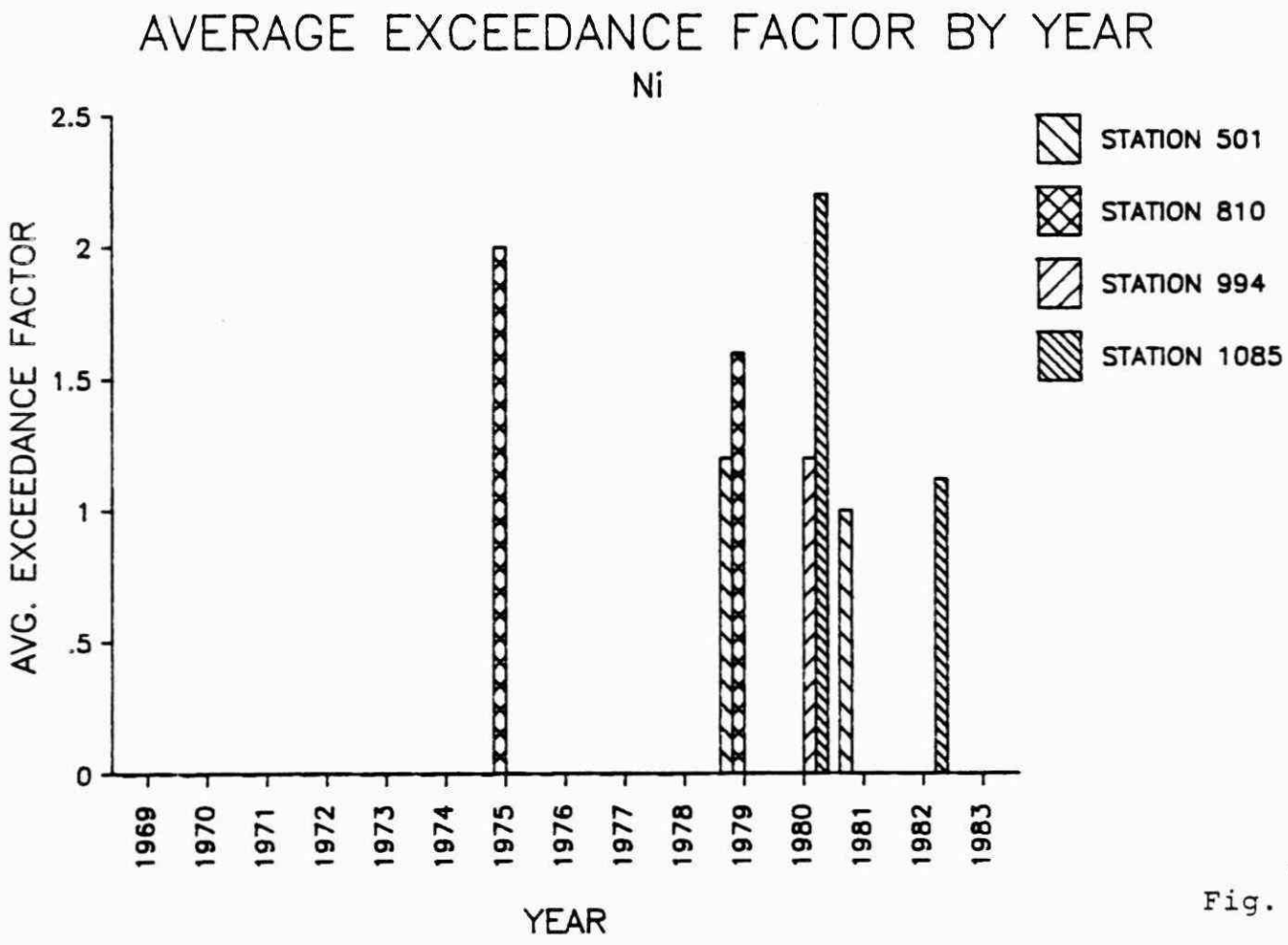
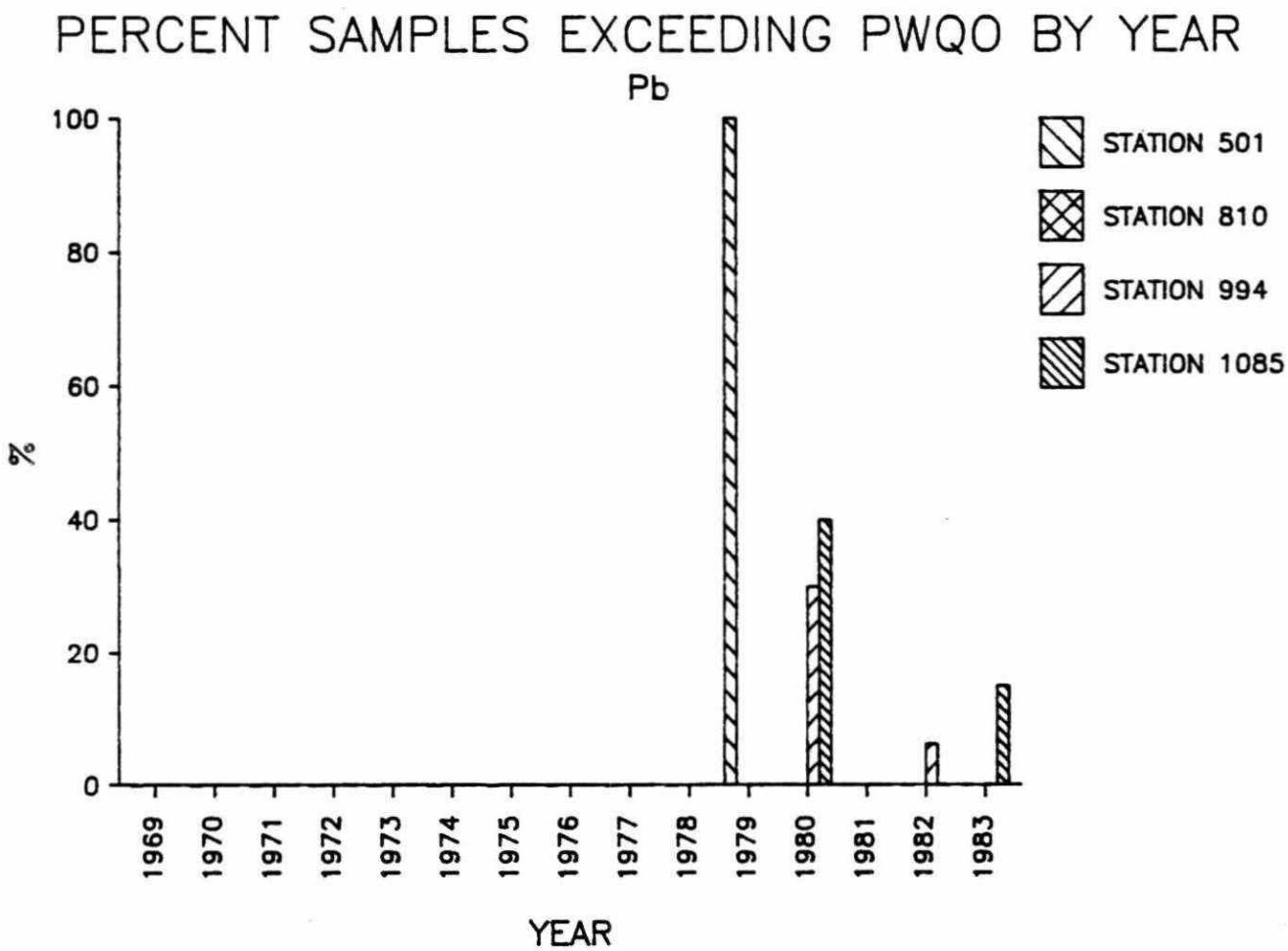

AVERAGE EXCEEDANCE FACTOR BY YEAR
Ni
2.5
2
1.5
1
.5
0
AVG. EXCEEDANCE FACTOR
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983
YEAR
STATION 501
STATION 810
STATION 994
STATION 1085

Fig. 15


PERCENT SAMPLES EXCEEDING PWQO BY YEAR
Pb
100
80
60
40
20
0
%
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983
YEAR
STATION 501
STATION 810
STATION 994
STATION 1085

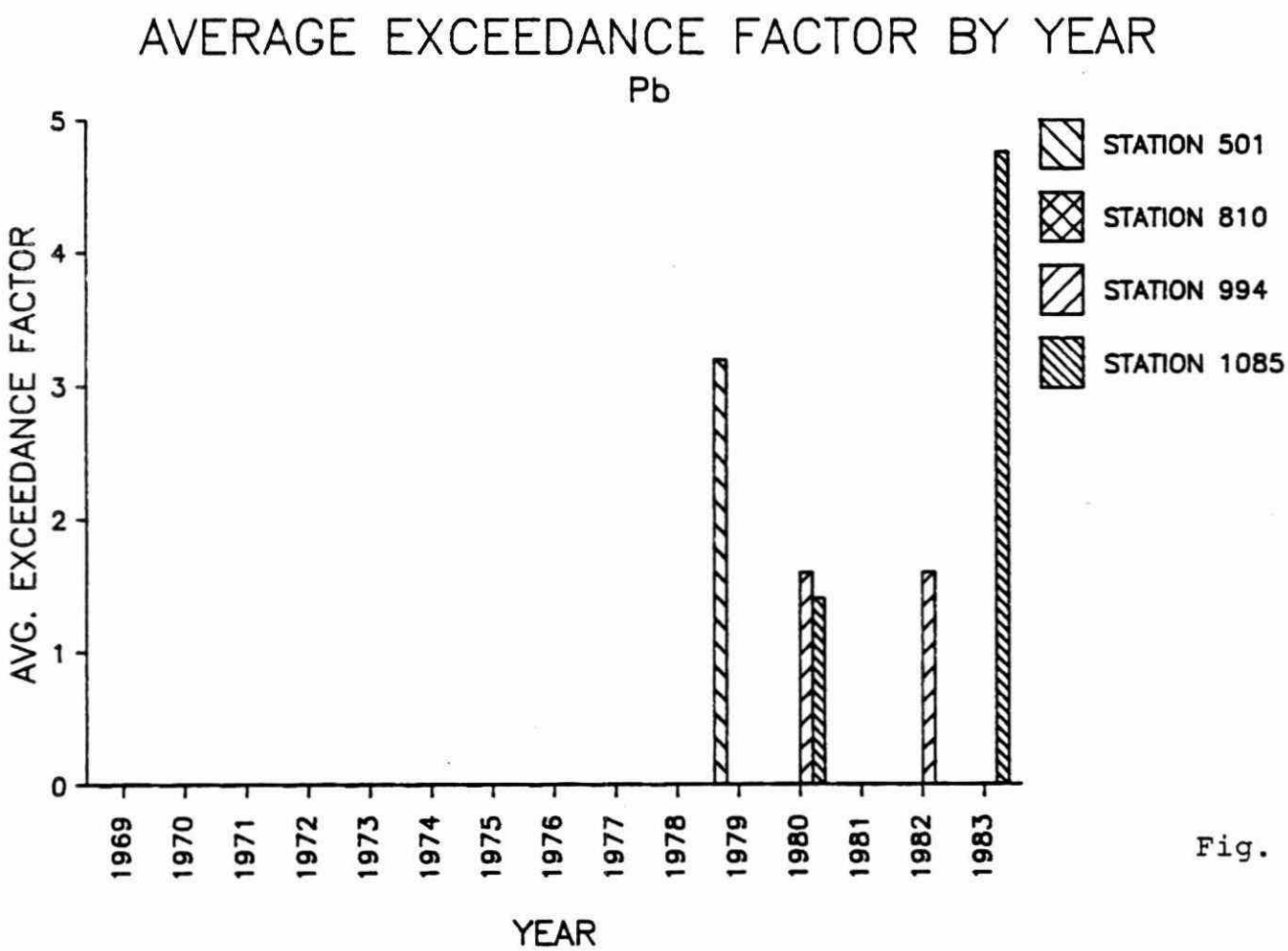
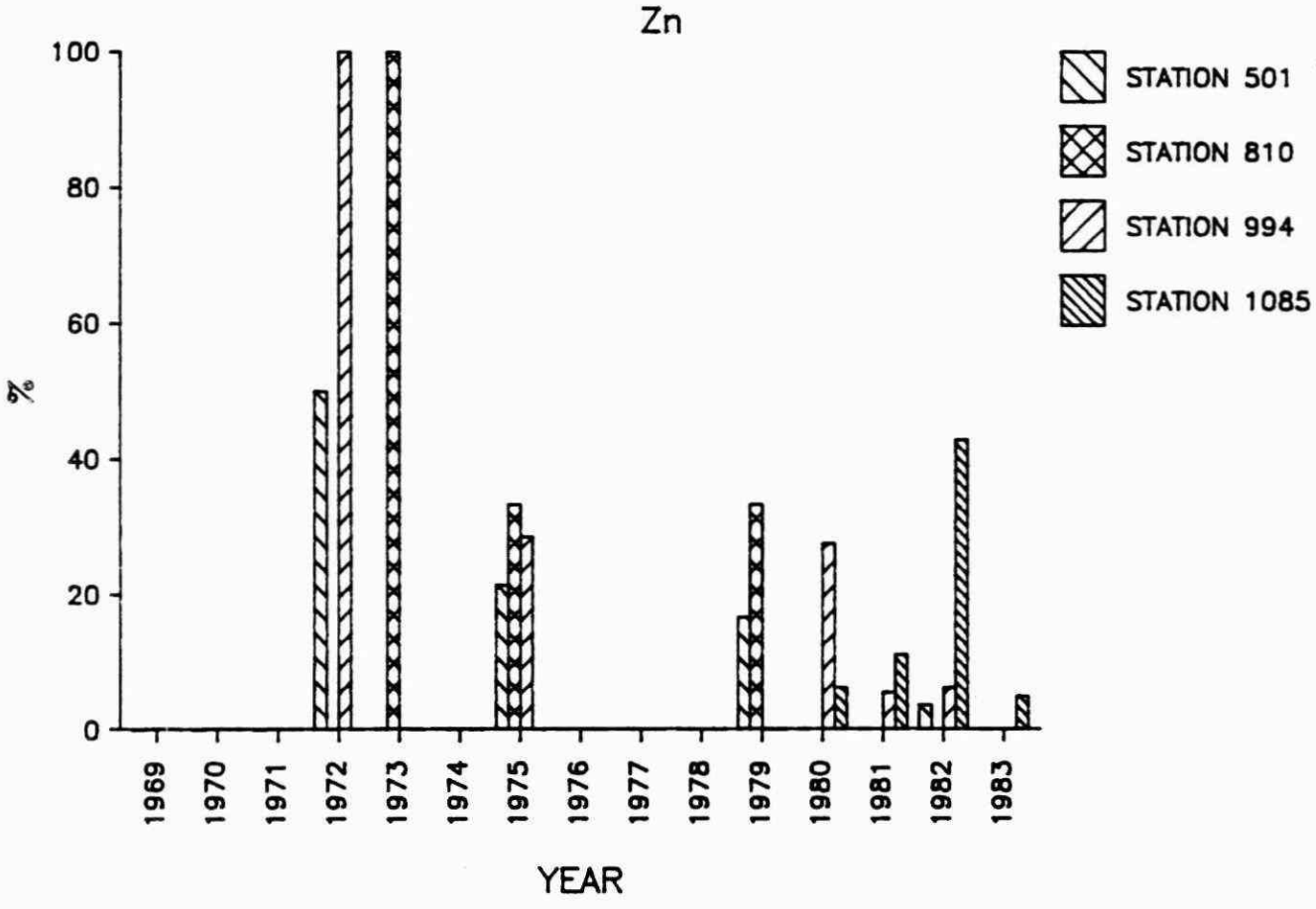

AVERAGE EXCEEDANCE FACTOR BY YEAR
Pb
5
4
3
2
1
0
AVG. EXCEEDANCE FACTOR
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983
YEAR
STATION 501
STATION 810
STATION 994
STATION 1085

Fig. 16


PERCENT SAMPLES EXCEEDING PWQO BY YEAR
Zn
100
80
60
40
20
0
%
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983
YEAR
STATION 501
STATION 810
STATION 994
STATION 1085

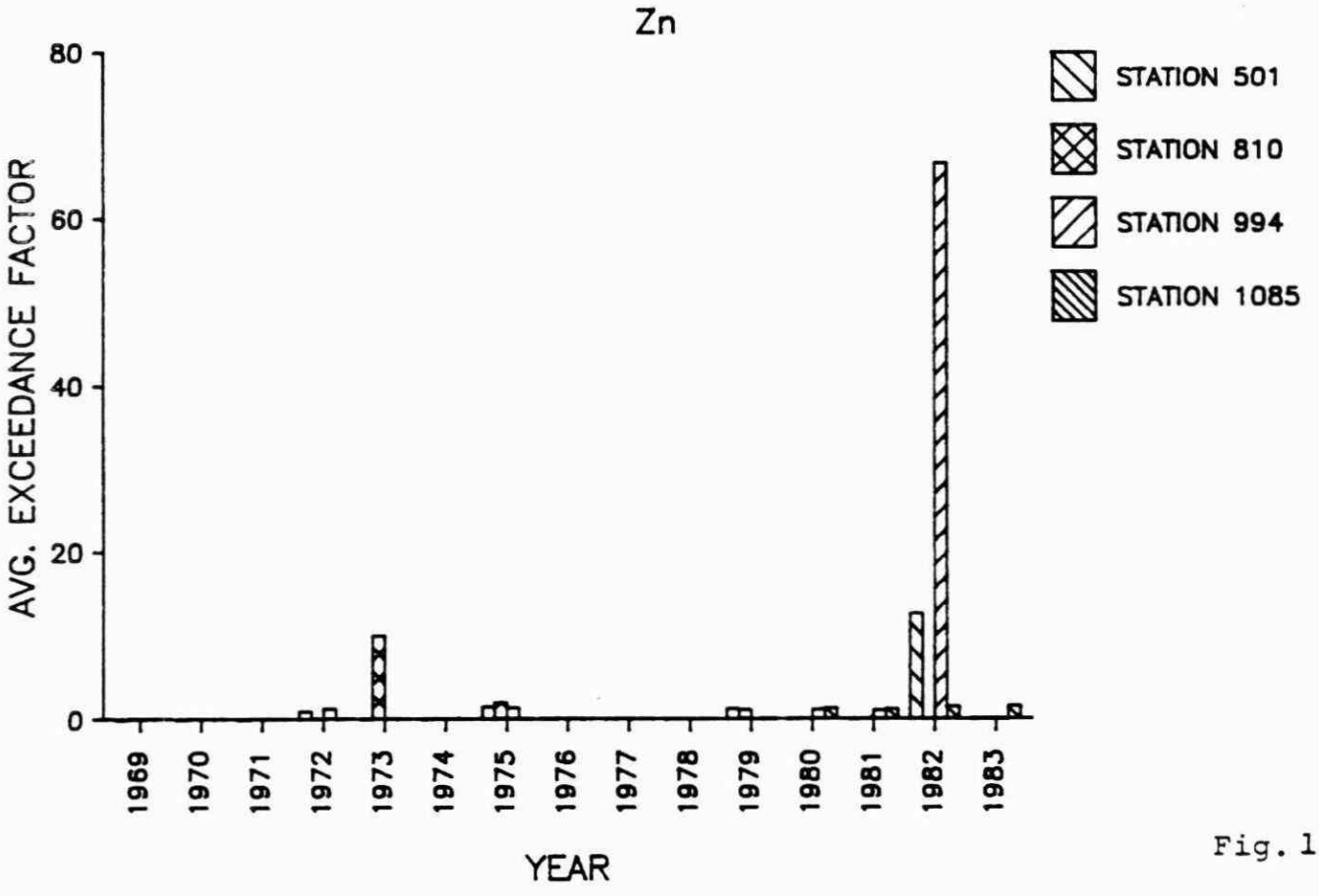

AVERAGE EXCEEDANCE FACTOR BY YEAR
Zn
80
60
40
20
0
AVG. EXCEEDANCE FACTOR
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983
YEAR
STATION 501
STATION 810
STATION 994
STATION 1085

Fig. 17

exceedance factors were also usually highest at Station 1085. In the early years of monitoring, percentage exceedance and average exceedance factors were generally highest at Station 994, which is the station farthest west. This station is also in fairly shallow water. The highest percentage exceedances and average exceedance factors observed during the monitoring program occurred at Station 994, which raises questions about this station's suitability as a control.

The trace metal measured most often was iron. In the earlier years of monitoring, the station with the most exceedances was 810. In the later years, it was 1085.

The other trace metals were measured infrequently before 1978. The metal that exceeded its PWQO most often was copper. The metal exceeding least often was chromium. Cadmium showed the highest average exceedance factors.

3.4 - Trend Analysis

The time series plots, Tukey smooth plots, box-and-whisker plots, and estimated annual averages produced from the Nanticoke data are included in Appendix C.

Table 11 summarizes the results of the seasonal Mann-Kendall test for trends in monthly median values. Table 12 gives the significance levels of combined Kendall tests performed to confirm the presence of the trends suggested by the results of the seasonal Mann-Kendall test. Table 13 gives the results of the Mann-Kendall trend tests on annual average values estimated with a regression model.

TABLE 11

Trends In Monthly Median Values
by the Seasonal Mann-Kendall Test

Parameter	April	May	June	July	August	September	October	November	December
Turbidity	x x	x x	-10 -10	x x	x x	x +10	x x	x x	+5 x
	x x x	x x -5	-10 x -10	-1 x x	-5 x x	x x x	-10 x x	x x x	x x x
Conductivity,	-5 -10	-1 -5	-1 -1	-0.1 -1	-0.1 -5	-0.1 x	-0.1 -5	-0.1 -5	-5 -0.1
25°C	-5 x x	-1 -10 x	-0.1 x x	-0.1 x x	-0.1 x x	-0.1 x x	-0.1 x	-0.1 x -10	-10 -10 x
Laboratory pH	x x	+10 x	x x	x x	x x	x x	x x	x	
	x	x	x	x	x	x	x x x	+5	x
Chloride	-1 -1	-1 -1	-5 -10	-0.1 -1	-1 -1	-1 -1	-5 -1	-1 -0.1	
	-5	-0.1	-10	-1	-1	-1	-1	-0.1	
Ammonium, total	x x	-5 -5	x x	x x	x x	x x	-10 -1	x x	x
	x x x	x x	x x x	x x x	x x	x x x	-10 0 -5	x x	x -5 0
Nitrogen, total	x x	x x	x x	x x	x	x x	+5 x	x x	
Inorganic	x x	x -0.1	x x	x x	x	x x	+10 x	x	x
Nitrogen, total	x x	x x	x x	-10 x	x x	x x	x -5	x -5	-10
Kjeldahl	x x x	-10 x x	x x x	x x x	x x x	x x x	-10 x x	x +10 x	x -5
Kjeldahl organic	x x	-10 x	x x	x x	x x	x x	x -5	x -10	-5
Nitrogen	x x x	x x x	x x x	x x x	x x x	x x +5	x x x	x +10 x	-10 -10 -10
Chlorophyll-a,	x +10	x x	x x	x x	x x	x x	x x	x x	x x
total	x x x	x x x	-1 -10 -0.1	x -5 -10	x x x	x x x	x x x	x x	x x x
Chlorophyll-b,	x x	x x	x +5	x x	x +10	+5 +10	x x	x x	x
Total	+10 x	x -10 x	x x	x x	x x x	x x	x x	x x	x x

TABLE 11-2

Trends in Monthly Median Values
by the Seasonal Mann-Kendall Test

Parameter	April	May	June	July	August	September	October	November	December
Phosphate, fil-	-10 x	-1 x	x x	-10 x	x x	x x	x x	x -5	-0.1
tered reactive	x x x	-10	x x	-5 x	x x x	x x	-5 x x	-5 x	-10 x
Phosphorus, un-	-5 x	x -10	x x	x x	x x	x x	x -1	x -5	x -10
filtered total	x x	-10 x x	-1 -10 -10	x x	-5 x x	x x x	-10 x	-5 +10	x x x
Iron, unfiltered	x x	x x	x x	x x	-5 x	-10 x	x -5	x x	x
Total	x x x	-5 -10 x	-5 x x	-5 x x	x -10 -10	x x x	x x x	x x x	x x x

LEGEND

501 810 - order of stations
994 1085 1086

A numeral indicates the significance level, 10, 5, 1 or 0.1%.
An x denotes a result not significant at 10%.
A blank indicates insufficient data.
The sign indicates the direction of the trend.

TABLE 12

Significance Levels of Combined Kendall Tests for Trend

Parameter	Station Number 501	810	994	1085	1086
Turbidity	10,x	x,x	1,5	x,x	x,x
Conductivity, 25°C	0.1,0.1	0.1,0.1	0.1,0.1	x,x	x,x
Laboratory pH	x,x	x,x	x,x	x,0.1	x,x
Chloride	0.1,0.1	0.1,0.1	0.1,0.1		
Ammonium, total	0.1,10	1,5	5,x	x,x	x,x
Nitrogen, total inorganic	x,x	x,x	x,x	x,0.1	
Nitrogen, total Kjeldahl	1,x	x,1	10,x	5,x	x,10
Kjeldahl organic nitrogen	5,x	x,10	x,x	x,x	x,10
Chlorophyll-a	x,x	5,x	10,x	10,x	x,0.1
Chlorophyll-b	1,x	0.1,10	x,x	x,x	x,x
Phosphate, filtered reactive	0.1,0.1	5,x	0.1,1	x,x	x,x
Phosphorus, unfiltered total	0.1,10	10,5	0.1,1	x,x	x,x
Iron, unfiltered total	0.1,5	x,10	1,5	x,x	x,x

LEGEND

First entry: Combined Score Method
Second entry: Fisherian Combination
A numeral indicates the significance level, 10, 5, 1 or 0.1%.
An x denotes a result not significant at 10%.
A blank indicates insufficient data.

TABLE 13

Mann-Kendall Trend Test
on Estimated Annual Values

Parameter	Station Number 501	810	994	1085	1086
Turbidity	x	-5	x	x	x
Conductivity, 25°C	-0.1	-1	-0.1	x	x
Laboratory pH	x	x	x	x	x
Chloride	-0.1	-0.1	-0.1	x	x
Ammonium, total	x	x	x	x	x
Nitrogen, total inorganic	x	x	x	x	x
Nitrogen, total Kjeldahl	-1	-1	x	x	-10
Kjeldahl organic nitrogen	-5	-5	x	+5	-10
Chlorophyll-a	x	x	x	x	-5
Chlorophyll-b	x	x	x	x	x
Phosphate, filtered reactive	-1	-5	-0.1	-10	-0.1
Phosphorus, unfiltered total	-5	x	-1	x	x
Iron, unfiltered total	-10	x	-0.1	x	x

LEGEND

A numeral indicates the significance level, 10, 5, 1 or 0.1%.
An x denotes a result not significant at 10%.
The sign indicates the direction of the trend.

These results reveal marked decreases for conductivity and chloride at Stations 501, 810, and 994. Less pronounced decreases are suggested for total ammonium, total Kjeldahl nitrogen, Kjeldahl organic nitrogen, filtered reactive phosphate, total phosphorus and iron, primarily at these same three stations. For turbidity, laboratory pH, inorganic nitrogen, chlorophyll-a and chlorophyll-b, there is no unequivocal evidence of trend in these results.

The seasonal Mann-Kendall tests suggest that there are incresing trends in some months at some stations for turbidity, laboratory pH, inorganic nitrogen, Kjeldahl organic nitrogen, and chlorohpyll-b. These few apparently increasing trends, however, are not nearly as widespread over months and stations as are the decreasing trends revealed by the seasonal Mann-Kendall tests.

Table 14 gives the results of comparing shallow and deep values recorded at the same time and location. For most of the parameters at Stations 501 and 994, the median at the shallow depth is less than the median at the deeper depths and the variances are often different. At Stations 810 and 1086, however, the medians and variances appear to be the same at the shallow and deep depths for most of the parameters, suggesting greater vertical mixing at these two stations.

Table 15 shows the result of using the Kruskal-Wallis test and one-way analysis of variance to compare means between and within samples with replicates. The only parameters for which appreciable numbers of replicates are available are total Kjeldahl nitrogen, total phosphorus and iron. For total phosphorus and iron the means among replicated samples are significantly different from each other across all stations. There appears to be more unformity among means of replicated samples for total Kjeldahl nitrogen. The observed differences among means could be caused by seasonality, trend

TABLE 14

Comparison of Shallow (X) and Deep (Y) Values

Parameter	Station Number 501	810	994	1086
Turbidity	-1,+5	x,x	-0.1,x	-10,x
Conductivity, 25°C	-0.1,x	x,x	-10,x	,x
Laboratory pH	+1,x	x,-0.1	x,x	+5,x
Chloride	x,x	x,x	+5,+1	,-5
Ammonium, total	-1,x	x,x	-5,-0.1	x,+5
Nitrogen, total inorganic	-0.1,-0.1	x,-0.1	-10,-0.1	x,x
Nitrogen, total Kjeldahl	x,+0.1	x,x	-5,x	x,x
Kjeldahl organic nitrogen	x,+0.1	x,x	-5,x	x,x
Chlorophyll-a	-5,+0.1	-0.1,x		
Chlorophyll-b	-10,x	x,x		
Phosphate, filtered reactive	-5,-0.1	x,x	x,+0.1	x,x
Phosphorus, unfiltered total	x,-0.1	-1,-1	-1,+0.1	x,+10
Iron, unfiltered total	-0.1,-5	x,x	x,-0.1	x,x

LEGEND

First entry: Wilcoxon test for equality of medians of paired X and Y
Second entry: Pitman test for equality of variances of paired X and Y.
A numeral indicates the significance level, 10, 5, 1 or 0.1%.
An X denotes a result not significant at 10%.
A blank indicates insufficient data.
For Wilcoxon test, + indicates median of X > median of y and
- indicates median of X < median of Y.
For Pitman test, + indicates variance of X > variance of Y and
- indicates variance of X < variance of Y.

TABLE 15

Comparison of Means
Between and Within Samples

Parameter	Station Number 501	994	1085	1086
Turbidity	10,10(8)	x,5(3)		x,5(3)
Conductivity, 25°C	x,x(8)	x,0.1(3)		0.1,0.1(3)
Laboratory pH		x,x(3)		x,5(3)
Ammonium, total	x,x(16)	10,5(10)	x,x(5)	x,5(8)
Nitrogen, total inorganic		x,5(3)		x,1(3)
Nitrogen, total Kjeldahl	1,10(51)	x,x(26)	10,0.1(23)	x,10(25)
Kjeldahl organic nitrogen	x,x(15)	10,0.1(9)	x,x(5)	5,1(8)
Chlorophyll-a	x,x(8)			
Chlorophyll-b	x,5(8)			
Phosphate, filtered reactive		x,x(3)		x,x(3)
Phosphorus, unfiltered total	0.1,5(51)	0.1,0.1(27)	0.1,0.1(22)	1,0.1(24)
Iron, unfiltered total	0.1,0.1(53)	0.1,0.1(32)	0.1,0.1(28)	0.1,0.1(32)

LEGEND

First entry: Kruskal-Wallis Test
Second entry: Analysis of Variance
Third entry: (n) gives the number of replicates available.
A numeral indicates the significance level, 10, 5, 1 or 0.1%.
An x denotes a result not significant at 10%.
A blank indicates insufficient data.

or depth differences. Seasonality could be the main reason for the differences in means, but more data would be required to test this hypothesis.

3.5 - Loadings

Figure 18 shows estimated annual loadings of several parameters to Long Point Bay from the industries and tributaries at Nanticoke. The industrial loadings appear to be appreciably higher than the tributary loadings for most of these parameters; however, this is probably an artifact of the analytical procedures. The creek samples were analyzed by the MOE and the industrial effluent samples were analyzed by the industries themselves. Analytical detection limits reported by these various laboratories were not all the same. When concentrations reported as detection limits were used in loadings calculations, they were assumed to be at the detection limit. Consequently, many of the loadings, especially those reported by Stelco and Texaco, are probably overestimates stemming from the higher detection limits of their laboratories.

Only the loadings estimated for Nanticoke Creek can be assumed to be reasonably accurate. Discharge in this stream is measured continuously by WSC. Water quality is monitored approximately monthly by the MOE, and the method used to estimte Nanticoke Creek annual loadings was the ratio estimator recommended by the International Joint Commission for computing tributary loadings to the Great Lakes.

Figure 19 shows annual discharge volumes and loadings of residue particulate, iron and total phosphorus in Nanticoke Creek during the 15 years of nearshore water quality monitoring at Nanticoke. The annual discharge volume increased at an average rate of 1.96 Mm^3/yr. The slopes of lines fit to the data for residue particulate, iron, and total phosphorus,

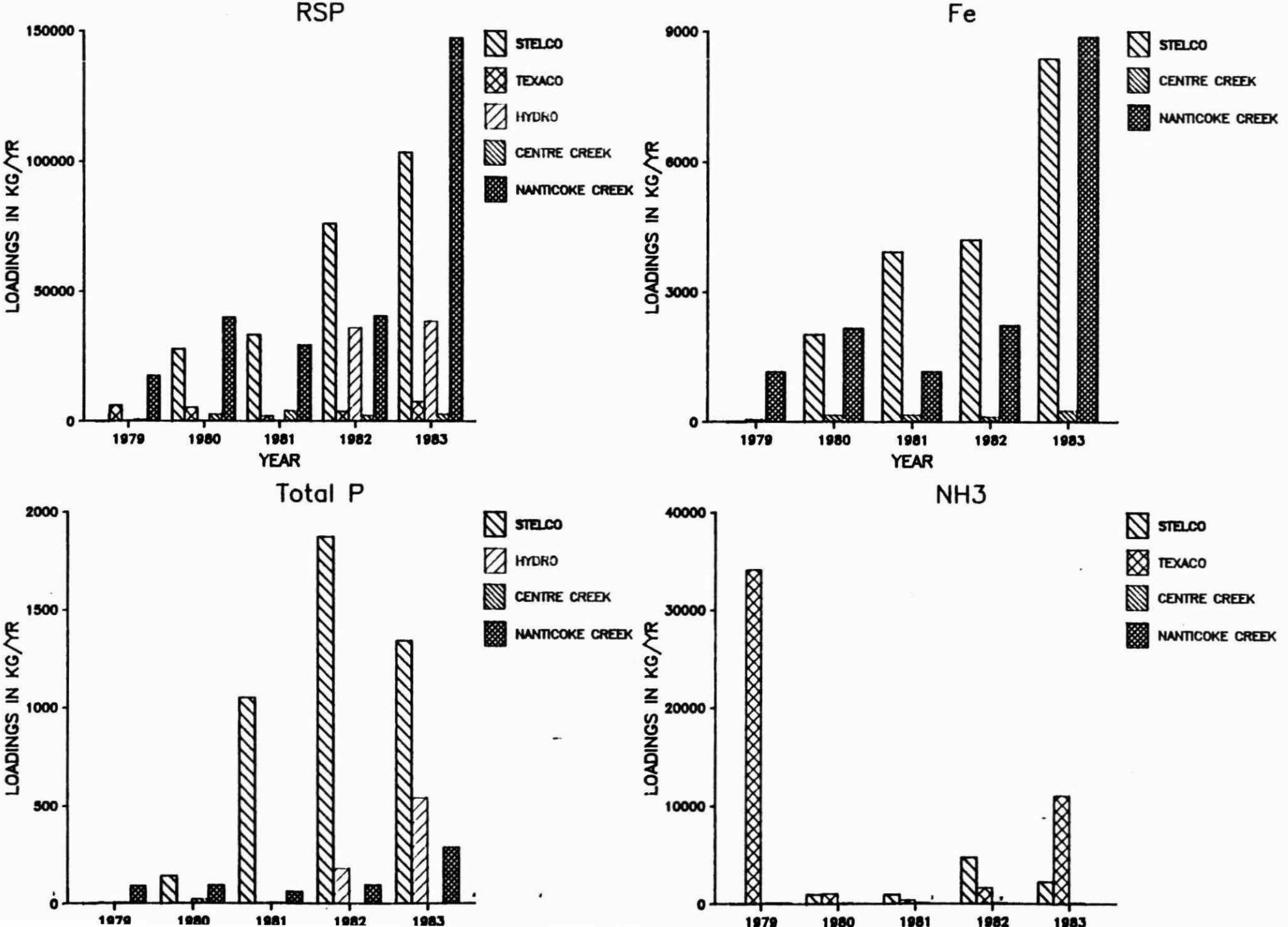
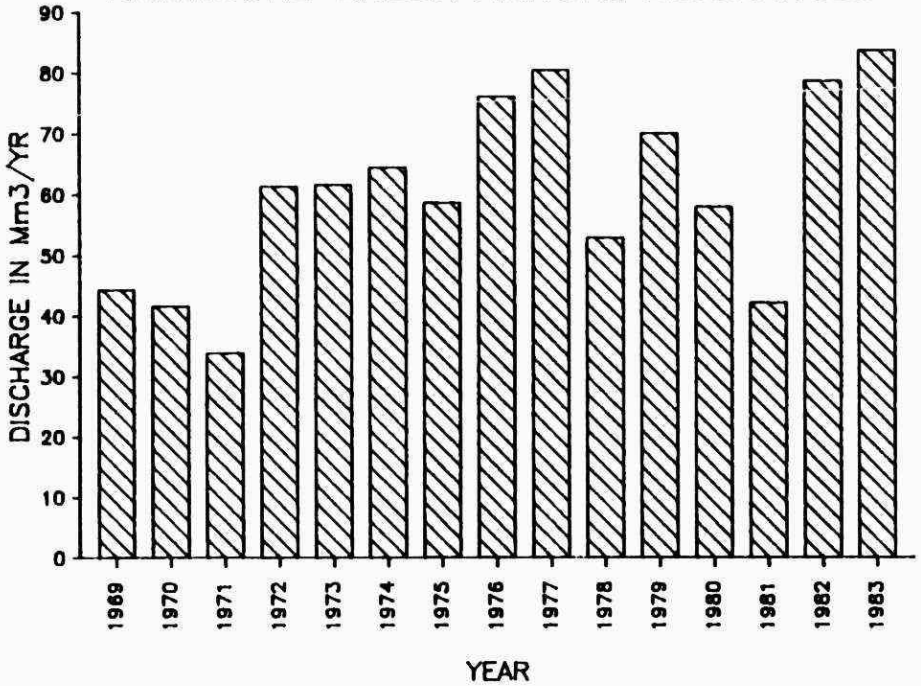
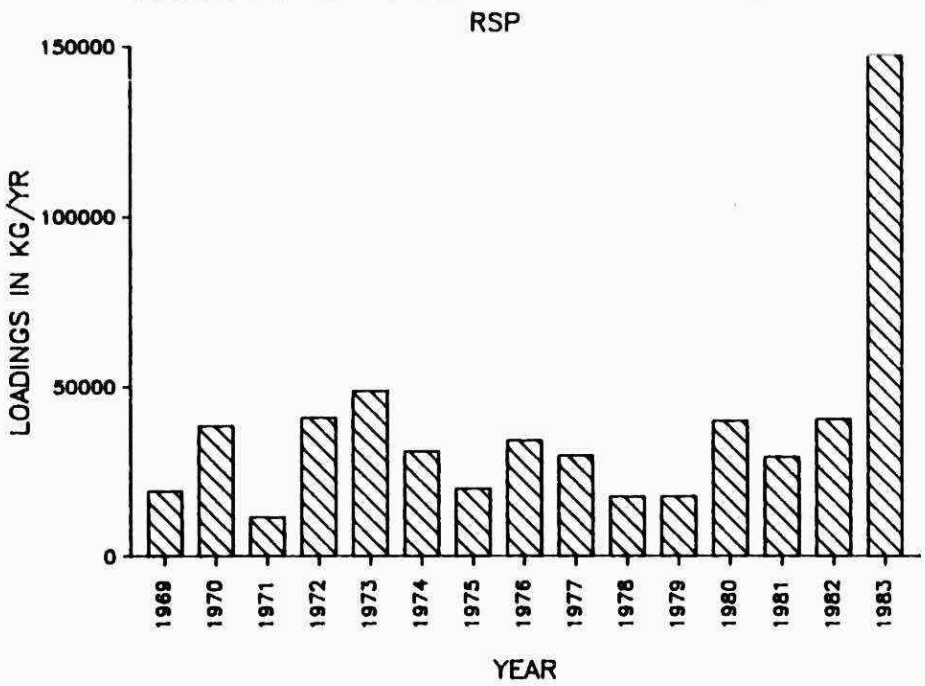

RSP
LOADINGS IN KG/YR
150000
100000
50000
0
1979
1980
1981
1982
1983
YEAR
STELCO
TEXACO
HYDRO
CENTRE CREEK
NANTICOKE CREEK
Fe
LOADINGS IN KG/YR
9000
6000
3000
0
1979
1980
1981
1982
1983
YEAR
STELCO
CENTRE CREEK
NANTICOKE CREEK
Total P
LOADINGS IN KG/YR
2000
1500
1000
500
0
1979
1980
1981
1982
1983
STELCO
HYDRO
CENTRE CREEK
NANTICOKE CREEK
NH3
LOADINGS IN KG/YR
40000
30000
20000
10000
0
1979
1980
1981
1982
1983
STELCO
TEXACO
CENTRE CREEK
NANTICOKE CREEK

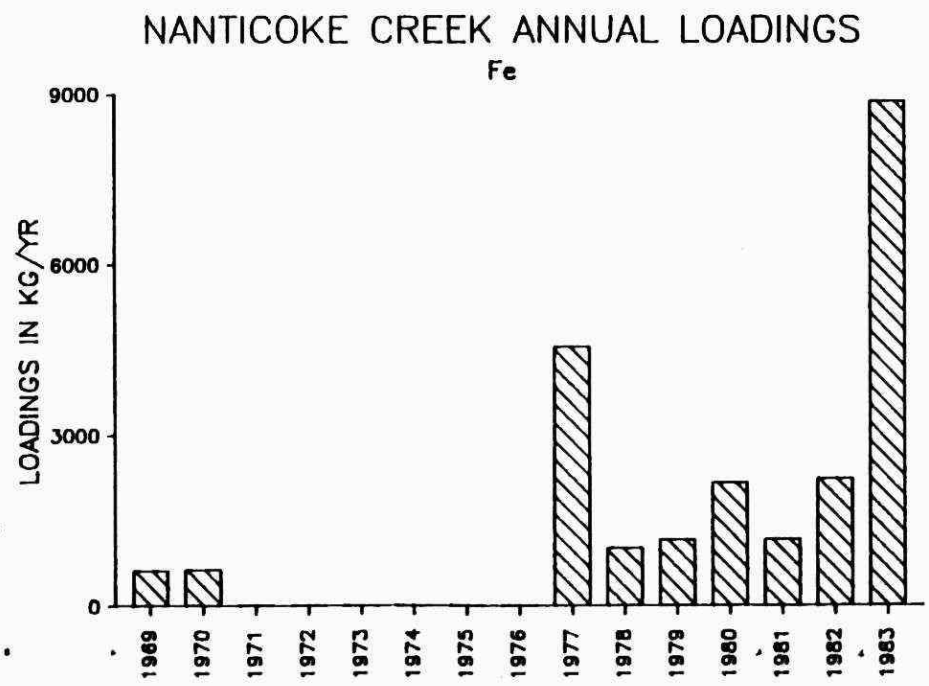
Fig. 18

Phenols
LOADINGS IN KG/YR
0
20
40
60
80
100
YEAR
1979
1980
1981
1982
1983
STELCO
TEXACO
CENTRE CREEK
NANTICOKE CREEK
CN
LOADINGS IN KG/YR
0
300
600
900
YEAR
1979
1980
1981
1982
1983
STELCO
CENTRE CREEK
NANTICOKE CREEK

Fig. 18 (Cont'd)


NANTICOKE CREEK ANNUAL DISCHARGES
DISCHARGE IN Mm3/YR
0
10
20
30
40
50
60
70
80
90
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983
YEAR


NANTICOKE CREEK ANNUAL LOADINGS
RSP
LOADINGS IN KG/YR
0
50000
100000
150000
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983
YEAR


NANTICOKE CREEK ANNUAL LOADINGS
Fe
LOADINGS IN KG/YR
0
3000
6000
9000
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983

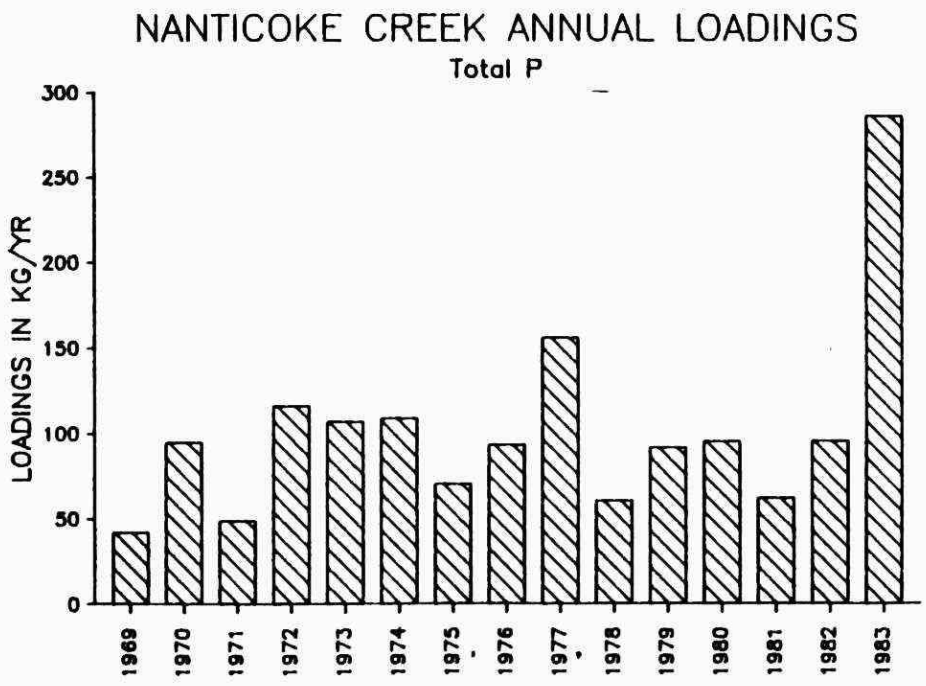

NANTICOKE CREEK ANNUAL LOADINGS
Total P
LOADINGS IN KG/YR
0
50
100
150
200
250
300
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983

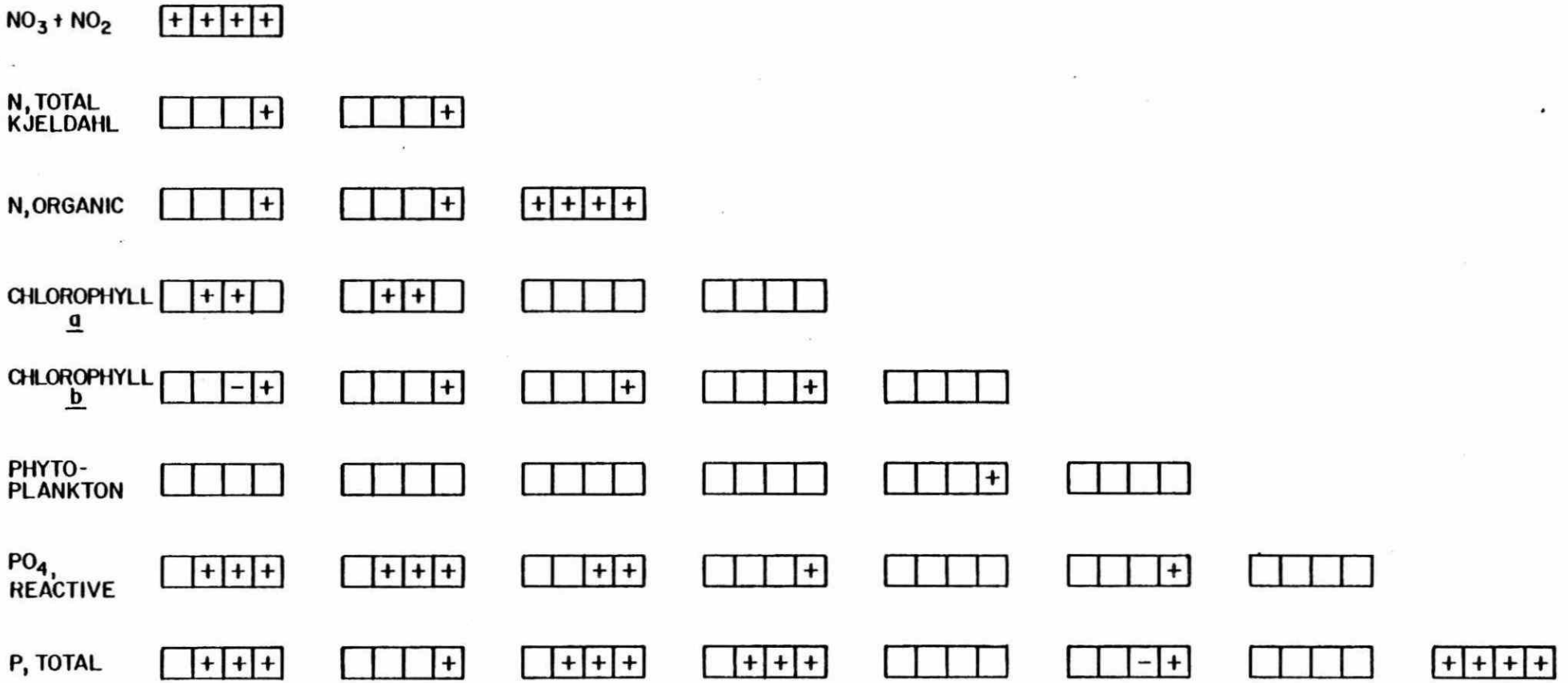
Fig. 19

however, are not significantly different from zero at the 95% confidence level. Note that the loadings of these three parameters were quite high in 1983, whereas the disharge volume was not much higher in 1983 than in previous years. It is not possible at this time to determine whether this is the beginning of a trend in Nanticoke Creek loadings to Lake Erie.

3.6 - Correlations

Figure 20 is a correlation matrix for phytoplankton biomass, chlorophyll, and nutrients in the Nanticoke area of Lake Erie. This matrix shows the results of correlation analysis of data set 2 (see Table 7, Section 2.5.6). This data set contains almost half again as many observations as data set 1 and it includes the chlorophyll data that were omitted from data set 3. Data set 2 thus represents the best compromise between the largest number of observations and the largest number of parameters.

Figure 20 shows that phytoplankton biomass is not significantly correlated with any of the other parameters. The only correlation of phytoplankton is with chlorophyll-a at Station 1085. These two parameters would normally be expected to be correlated at the other stations as well; however, the water samples analyzed for chlorophyll were near-surface grab samples and those analyzed for phytoplankton biomass were photic zone composite samples (Hopkins and Lea, 1982). Hence the chlorophyll values need not necessarily be directly related to the phytoplankton values. Station 1085 is the shallowest of the four stations, so it is more likely to be well mixed, causing the chlorophyll grab sample to be more or less representative of the entire photic zone. Note also that virtually all the other parameters are correlated with each other at Station 1085. Perhaps the shallowness of this station, or its nearness to the mouth of



LEGEND

501 810 — 994 / 1085 ORDER OF STATIONS

\+ POSITIVE CORRELATION AT 95% LEVEL

\− NEGATIVE CORRELATION AT 95% LEVEL

NO SIGNIFICANT CORRELATION AT 95% LEVEL

FIG. 20

MINISTRY OF THE ENVIRONMENT
NANTICOKE WATER QUALITY

CORRELATION MATRIX

ACRES

Centre Creek, causes levels of most parameters to change simultaneously with changes in nearshore turbulence or Centre Creek discharge.

At Stations 501, 810 and 994, the most prevalent correlations are basically those required by the chemistry of the parameters

- total inorganic nitrogen with nitrate plus nitrite
- total Kjeldahl nitrogen with organic nitrogen
- reactive phosphate with total phosphorus.

At Stations 810 and 994, there are also correlations between some of the nitrogen and phosphorus parameters and between some of the nitrogen parameters and chlorophyll-a. These correlations are lacking at Station 501, which is the farthest offshore of the four stations.

This correlation analysis was undertaken primarily to establish the correlations between phytoplankton biomass and other parameters that influence phytoplankton growth. These correlations are not found in the Nanticoke data. This might be because the water samples and phytoplankton samples were collected differently. It may also be because the relationship between a nutrient concentration and phytoplankton biomass is not necessarily revealed by correlation of simultaneous measurements. The predictive relationships used in recent years by lake managers have generally been between average values, such as total phosphorus concentration at spring overturn and average summer chlorophyll-a (Dillon and Rigler, 1974). In either event, the Nanticoke data do not seem to warrant further investigation with the zero lag correlation analysis technique. Trends in chlorophyll and nutrient concentrations were studied by other methods as discusssed in Section 3.4.

3.7 - Metals Statistics

In general, the lognormal distribution gave an adequate to good fit to the Nanticoke trace metals data (Figure 21) according to the χ^2 goodness-of-fit test.

Means of cadmium, chromium, nickel and lead data sets were generally below detection limits, so these data could not be fit to a distribution.

The data for copper, iron, and zinc are generally lognormally distributed. Most of the questionable fits to a lognormal distribution occurred when many low values clustered near the detection limit. This made it difficult to resolve the data into classes, so the χ^2 value was quite sensitive to subjective interpretation. In addition, some of the instances of rejection of the lognormal distribution were caused by one, or a few, very high concentrations that had a disproportionate influence on the χ^2. Given the preponderence of instances when the copper, iron, and zinc data were adequately fit to the lognormal distribution, it appears that this distribution is, on the whole, reasonable for these parameters.

Copper, iron, and zinc means from five stations were tested by a t-test to determine whether samples collected in different years at one station are likely to have come from the same population. With a few exceptions, the samples obtained in 1980 to 1983 at any one of these stations appear to have been drawn from a single population (Figure 22).

At Station 501 and at Station 994, copper samples in different years from 1981 to 1983 appear to have come from a single population.

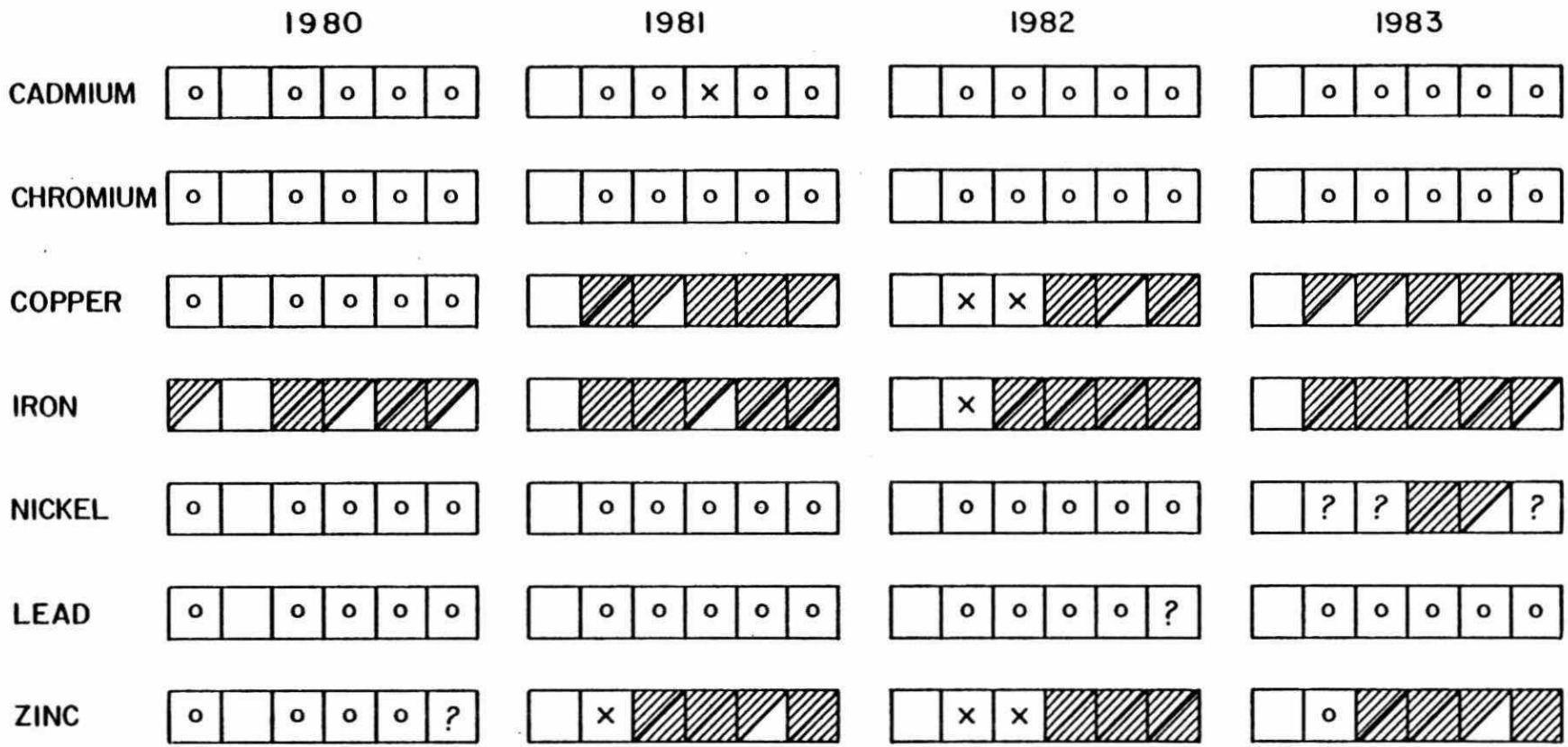


FIG. 21

MINISTRY OF THE ENVIRONMENT
NANTICOKE WATER QUALITY

ACRES

FIT OF TRACE METAL DATA TO LOGNORMAL DISTRIBUTION

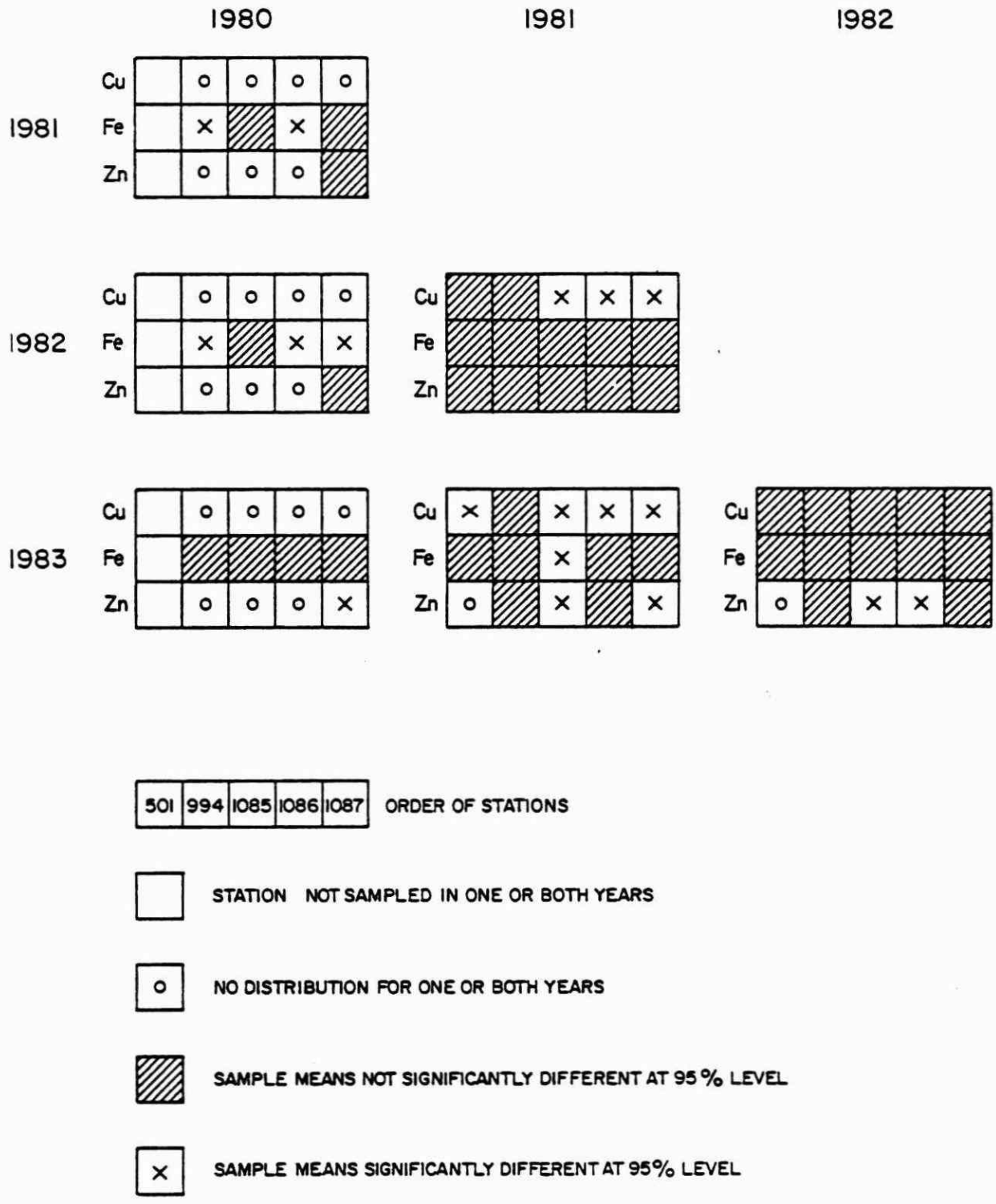


FIG.22

MINISTRY OF THE ENVIRONMENT
NANTICOKE WATER QUALITY

COMPARISON OF TRACE METAL SAMPLE MEANS

ACRES

At Stations 1085, 1086 and 1087, however, the copper samples obtained in 1981 appear to be drawn from different populations than were sampled in 1982 and 1983. These three stations are the ones closest to Centre Creek, so the differences in 1981 might have been caused by Stelco's effluents or by some other source in the Centre Creek watershed.

Iron samples appear to have been drawn from a single population in 1981 to 1983 at each of the five stations. The 1980 iron samples at Stations 994 and 1086, however, appear to be from different populations than were sampled in 1981 and 1982. Note that the 1980 and 1983 samples at these two stations seem to have been drawn from the same population, as do the 1981, 1982 and 1983 samples, so the apparently anomalous character of the 1980 samples might not be significant.

Samples of zinc also seem to have come from a single population in different years at each station, except that this tendency is less consistent at the three stations nearest the mouth of Centre Creek. The samples obtained in 1983 seem to be from different populations at these stations. Perhaps Stelco's effluent or some other source on Centre Creek contributed to this difference.

3.8 - Trophic Conditions

Between 1910 and 1965, marked increases occurred in concentrations of sodium plus potassium, chloride, calcium, sulfate, and total dissolved phosphorus in Lake Erie (Beeton, 1965). In the western basin, the concentration of phosphate phosphorus increased about 4 to 10 times between 1942 to 1951 and 1963 to 1967 and the concentration of ammonia nitrogen increased over 10 times between 1930 and 1968 (International

Lake Erie Water Pollution Board and International Lake Ontario-St. Lawrence River Water Pollution Board, 1969). Similar information on trends in the eastern basin early in this century is not available; however, nutrient concentrations were generally lower in the eastern basin than in the western basin. By 1969, when the Nanticoke environmental studies began, the eastern basin as a whole was classified as oligotrophic to mesotrophic in trophic state.

Gregor and Rast (1982) developed a Composite Trophic Index (CTI) for Canadian nearshore waters. The CTI is based on paired linear relationships for Secchi disk depth, chlorophyll-a, and total phosphorus. The CTI developed for nearshore Lake Erie at Nanticoke with 1972 and 1973 data was 4.4, giving this region an oligotrophic/mesotrophic status.

New values for the CTI were computed with surface water quality data collected at Nanticoke during the summer months of 1982 and 1983 (Table 16). The indexes for the stations in deeper water (501, 994, 1086) were computed by the Gregor and Rast (1982) formula for the lower lakes. The indexes for the two stations in shallower water near the mouth of Centre Creek (1085 and 1987) were computed by this formula and also by the formula for turbid areas.

The CTI for combined data for Stations 501, 994 and 1086 is 4.0. This is slightly less than the value given by Gregor and Rast (1982), suggesting an improvement in nearshore water quality at Nanticoke during the 1970s. This is consistent with the conclusion of Dobson (1981) that the process of cultural eutrophication of Lake Erie appears to have been brought under control and reversed.

Water quality at Stations 1085 and 1087 is likely to be influenced more by sediment discharged by Centre Creek or resuspended from the lake bottom than is water quality at the

other three stations. Thus, the formula for turbid regions may be more appropriate for these two stations. This formula gives a CTI of 4.06, which again suggests recent improvement in Nanticoke water quality.

TABLE 16

COMPOSITE TROPHIC INDEXES FOR 1982-1983

Station	Secchi Disk Depth* (m)	Chlorophyll-a* (µg/L)	Total Phosphorus* (µg/L)	Composite Trophic Index
501	4.58	1.14	8.6	2.32**
994	2.99	1.25	32.0	5.90**
1085	1.75	1.66	15.7	6.70** 3.92***
1086	2.77	1.08	14.0	4.20**
1087	1.56	1.68	16.7	7.47** 4.21***
501, 994 and 1086 combined	3.45	1.16	18.2	4.00**
1085 and 1087 combined	1.66	1.67	16.2	7.05** 4.06***

* Arithmetic means of summer (mid-June to mid-September) surface (<2 m depth) values

** Computed with the Gregor and Rast (1982) formula for the lower lakes

***Computed with the Gregor and Rast (1982) formula for turbid regions.

4 - DISCUSSION

4.1 - Data Quality

An important consideration in any data analysis program is the quality of the chemical data generated by the analytical laboratory. Specific quality assurance/quality control studies were not conducted on the Nanticoke water samples, so the quality of the Nanticoke data cannot be assessed directly. An indirect assessment can be obtained, however, by referring to the results of quality assurance/quality control studies done by the MOE laboratory during the period of the Nanticoke monitoring program. Two kinds of studies are considered in this section: interlaboratory comparison studies involving the MOE laboratory and internal quality control studies conducted by the MOE Inorganic Trace Contaminants section.

4.1.1 - Interlaboratory Comparison

The Data Quality Work Group of the International Joint Commission Surveillance Subcommittee (1979) has conducted several interlaboratory comparison studies that involved the MOE Rexdale laboratory. In Study 21 most laboratories were found to analyze sulfate in natural water samples to the nearest 0.5 mg/L in the 0 to 30 mg/L range. No problems were found in chloride measurements except when a specific ion electrode probe was used. No agreement was reached on pH or specific conductance. Silica results were quite scattered in an earlier study. Study 22, of major ions and nutrients in natural water samples, found that most of the participating laboratories could competently analyze the major ions, calcium, magnesium, sodium, potassium, and chloride. Some difficulties were encountered with

alkalinity and sulfate. Agreement was not reached on pH and specific conductance values. Many laboratories experienced difficulty with reactive silicate and total Kjeldahl nitrogen. In Study 23, the majority of laboratories performed adequately for most of the trace metals analyzed, and cobalt and nickel were rather well done. Many of the laboratories had difficulty with the iron analyses. Studies 24 and 25 demonstrated improvement over the results of earlier studies for reactive silicate and total phosphorus measurements. The principal laboratories involved in open lake and nearshore surveillance were in agreement for total phosphorus.

The MOE Rexdale laboratory has also participated in several interlaboratory comparison studies conducted by Environment Canada using water samples from the lower Great Lakes (Table 17). Turbidity measured by the turbidimeter was found to be the most precise measurement of suspended matter (McGirr, 1974). Alkalinity, chloride, and sulfate determinations had coefficients of variation of less than 10%, whereas the coefficient of variation for nitrate was 25% (Carron and Aspila, 1978). Laboratories that determine total phosphorus on a regular basis demonstrated better precision and accuracy than did laboratories that do this analysis infrequently (Aspila and Carron, 1978). The trace metal data provided by laboratories that regularly analyze natural waters with low metal levels were quite acceptable (Carron and Aspila, 1976).

The Laboratory Services Branch of MOE has provided the results of their performance on two recent interlaboratory comparison studies conducted by the International

TABLE 17

RESULTS OF SOME INTERLABORATORY COMPARISON STUDIES ON WATER SAMPLES FROM THE LOWER GREAT LAKES

Source of Sample	Parameter	Coefficient of Variation (%)	Reference
Lake Ontario	Turbidity by Hach 2100	15	McGirr, 1974
	Turbidity by Hach 2100A	12	"
	Nonfilterable residue	37	"
	Filterable residue	7.0	"
Lake Erie	Alkalinity	3.4	Carron and Aspila, 1978
	Chloride	6.0	"
	Sulfate	8.9	"
	Nitrate	25	"
Niagara River	Total phosphorus	58	Aspila and Carron, 1978
Lake Ontario	Cadmium	87	Carron and Aspila, 1976
	Chromium	77	"
	Nickel	60	"
	Lead	70	"
Georgian Bay	Copper	23	"
	Iron	45	"
	Lead	77	"
	Zinc	109	"

Joint Commission (IJC) and Environment Canada. In each study, ten water samples were sent to several laboratories for analysis. Each laboratory analyzed the samples for several trace metals and reported the analytical results to the agency sponsoring the study for evaluation.

Table 18 repeats the sponsoring agency evaluations of the performance of the MOE Inorganic Trace Contaminants (I.T.C.) laboratory on these studies. Low biases were observed in the results for cadmium, chromium and zinc in the IJC intercomparison study, where "bias" indicates a systematic error due to the analytical method that causes the measured values to deviate from the true value. Performance for all the other parameters was judged satisfactory.

4.1.2 - Internal Quality Control

Results of recent internal quality control studies on water samples have been made available by the Laboratory Services Branch of MOE and are summarized in Table 19.

In this table, 'accuracy' refers to the agreement between the average of several measured values and the accepted, or 'true', value (MOE, 1983). Accuracy is estimated by analyzing standard reference materials and is reported as the ratio of the mean of the measured values to the accepted value, expressed as a percentage. For each of the seven trace metals in Table 19 the reported accuracy is better than 90%. Note however that each accuracy is less than 100%, which indicates a tendency to measure concentrations slightly less than actual concentrations.

TABLE 18

Inorganic Trace Contaminants (I.T.C.) Laboratory Results In Interlaboratory Studies On Water Samples

Parameter	I.T.C. Performance on IJC Interlaboratory Study 42 (1983) (16 labs; 10 samples)	I.T.C. Performance on Environment Canada Interlaboratory Study L-2 (1983) (20 labs; 10 samples)
Cadmium	Low bias	Satisfactory except for 1 high result
Chromium	Low bias	Satisfactory except for 1 very high result
Copper	1 low result 1 high result	Satisfactory
Iron	2 low results	Satisfactory
Nickel	Satisfactory	Satisfactory except for 1 very high result
Lead	Satisfactory except for 1 low result	Satisfactory
Zinc	Low bias	Satisfactory

TABLE 19

Inorganic Trace Contaminants
(I.T.C.) Laboratory Quality
Control Results For Water Samples

Parameter	I.T.C. Acuracy (%) (1985)	I.T.C. Detection Limit (mg/L) (1985)
Cadmium	94.4	0.0002
Chromium	96.7	0.001
Copper	98.6	0.001
Iron	92.9	0.003
Nickel	96.6	0.002
Lead	95.6	0.001
Zinc	92.7	0.001

Table 19 also gives the detection limit for the method used to analyze each trace metal. This detection limit is three times the standard deviation of low-range, within-run duplicates, where generally duplicates are broken down into three ranges: 0 to 20%, 20 to 50%, and 50 to 100% of full scale (MOE, 1983).

4.2 - Effects of Industrial Development at Nanticoke

Water quality changes in the nearshore area at Nanticoke might be related more to changes in the eastern basin as a whole than to local industrial development. Accordingly, in this section recent trends in eastern basin water quality are qualitatively compared with trends found in the Nanticoke data to ascertain whether lake-wide changes in water quality might be responsible for the observed trends.

Table 20 shows trends for several parameters in the eastern basin of Lake Erie during the period of the Nanticoke Water Quality Study. These results are based primarily on a statistical assessment of the Great Lakes Surveillance Program designed and implemented by the Canadian government (El-Shaarawi, 1984). Note that there is overall agreement between the trends observed at Nanticoke and those observed for the eastern basin as a whole, which suggests that water quality changes at Nanticoke have been caused by lake-wide changes rather than by industrial development at Nanticoke.

4.3 - Recommendations for Future Work

It was not possible to evaluate the quality of the Nanticoke data directly because no formal quality assurance/quality control studies were included in the Naticoke monitoring

TABLE 20

RECENT TRENDS IN EASTERN BASIN WATER QUALITY COMPARED WITH TRENDS AT NANTICOKE STATIONS

Parameter	Trend (El-Shaarawi, 1984 unless otherwise indicated)	Trend Observed at Nanticoke Stations 501, 810 and 994
Chlorophyll-a	decreasing between 1968 and 1980	no clear trend
Total phosphorus	decreasing since 1970*	decreasing
Soluble reactive phosphorus	dropped after 1977 when compared with pre-1973	decreasing
Nitrate + nitrite	increasing between 1971 and 1980	no clear trend
Ammonia	decreasing	decreasing
Turbidity	increased between 1969 and 1972	no clear trend
Chloride	decreased from 1960s levels**	decreasing

* Rathke and Edwards, 1985
** Sonzogni et al, 1983

program. It is recommended that formal quality assurance/quality control procedures be incorporated into future monitoring programs of this sort so the quality of the resulting data can be assessed directly and compared with the quality of data from other laboratories.

There was some inconsistency in the stations and depths sampled and in the parameters measured during the 15 years of the Nanticoke monitoring program. This inconsistency occasionally reduced the sizes of the data sets available for statistical testing, thereby reducing the discriminating ability of the test. It is recommended that, insofar as possible, a consistent monitoring plan be adhered to throughout studies of this sort.

The present study concluded that nearshore Nanticoke water quality during the 15 years of monitoring basically followed the generally improving trend in the water quality of the eastern basin as a whole. This qualitative correspondence could be studied further by fitting a regression model to one or more water quality parameters across stations in the Nanticoke area and stations in the eastern basin. However, since local industrial development seems not to have appreciably degraded nearshore water quality at Nanticoke, development of such a regression model would be outside the scope of the original Nanticoke water quality study. It is suggested as an interesting possibility for using the extensive Nanticoke data set in a broader research application.

5 - CONCLUSIONS

The following are the conclusions of this analysis of 15 years of water quality data from nearshore Lake Erie at Nanticoke, Ontario.

- Cluster analysis showed that Nanticoke water sampling stations can be clustered into a group of offshore stations and a group of nearshore stations.

- PWQO for several parameters were exceeded from time to time. Exceedances for pH and un-ionized ammonia were generally infrequent and small. Exceedances for total phosphorus and iron were most frequent and largest at nearshore stations, and total phosphorus and phenols exceedances seem to have declined during the 15 years of monitoring. Copper was the trace metal that exceeded its PWQO most often and chromium exceeded least often. Cadmium was the trace metal that exceeded its PWQO by the greatest amount.

- The following water quality parameters showed generally decreasing trends during the Nanticoke program

  - conductivity
  - chloride
  - total ammonium
  - total Kjeldahl nitrogen
  - Kjeldahl organic nitrogen
  - filtered reactive phosphate
  - total phosphorus
  - iron.

- Annual discharge volume of Nanticoke Creek increased at a rate of almost 2 Mm^3/yr, but annual loadings of residue particulate, iron, and total phosphorus to Lake Erie from Nanticoke Creek did not change appreciably over the 15 years of nearshore water quality monitoring.

- Phytoplankton biomass, chlorophyll, and nutrients were not significantly correlated in the Nanticoke data.

- As a rule, the lognormal distribution gave an adequate to good fit to Nanticoke trace metal data. With a few exceptions, trace metal samples obtained in different years from a station appeared to have been drawn from a single population.

- Nearshore trophic conditions improved at Nanticoke between 1972-73 and 1982-83.

- The trends observed in the Nanticoke water quality data were generally similar to trends reported in the literature for the eastern basin of Lake Erie as a whole.

BIBLIOGRAPHY

BIBLIOGRAPHY

Akaike, H. 1974. A new look at the statistical model identification. IEEE Trans. on Automatic Control, 19: 716-723.

Amik Resources Group. In preparation. Nanticoke Water Chemistry, 1981.

Aspila, K. I. and J. M. Carron. 1978. Interlaboratory Quality Control Study No. 15, Total Phosphorus in Natural Waters. Report Series No. 52. Burlington, Ontario: Environment Canada, Inland Waters Directorate.

Beeton, A. M. 1965. Eutrophication of the St. Lawrence Great Lakes. Limnol. Oceanogr. 10:240-254.

Box, G.E.P. and D.R. Cox, 1964. An analysis of transformations. Royal Statistical Society, Series B, 26: 211-252.

Carron, J. M. and K. I. Aspila. 1976. Interlaboratory Quality Control Study Nos. 12 and 13, Aluminum, Cadmium, Chromium, Cobalt, Copper, Lead, Iron, Manganese, Nickel and Zinc. Report Series No. 44. Burlington, Ontario: Environment Canada, Inland Waters Directorate.

Carron, J. M. and K. I. Aspila. 1978. Interlaboratory Quality Control Study No. 14, Major Ions: Calcium, Magnesium, Sodium, Potassium, Hardness, Alkalinity, Chloride, Sulphate, and Nitrate. Report Series No. 51. Burlington, Ontario: Environment Canada, Inland Waters Directorate.

Conover, W.J. 1971. Practical Nonparametric Statistics. New York: John Wiley.

Davis, J.C. 1973. Statistics and Data Analysis in Geology. New York: John Wiley and Sons.

Demal, L. A. and J. W. Tanner. In preparation. Nanticoke Water Chemistry, 1980.

Dillon, P. J. and F. H. Rigler. 1974. The Phosphorus-Chlorophyll Relationship in Lakes. Limnol. Oceanogr. 19:767-773.

Dobson, H.F.H. 1981. Trophic Conditions and Trends in the Laurentian Great Lakes. Water Quality Bull. 6(4): 146-151; 158; 160.

Dolan, D. M., Yui A. K. and R. D. Geist. 1981. Evaluation of River Load Estimation Methods for Total Phosphorus. J. Great Lakes Res. 7(3):207-214.

El-Shaarawi, A. H. 1984. Statistical Assessment of the Great Lakes Surveillance Program, 1966 - 1981, Lake Erie. Burlington, Ontario: Environment Canada, Inland Waters Directorate.

Fisher, R.A. 1970. Statistical Methods for Research Workers. Edinburg: Oliver and Boyd.

Fraser, A. S. and K. E. Willson. 1981. Loading Estimates to Lake Erie, 1967 - 1976. Scientific Series No. 120. Burlington, Ontario: Environment Canada, Inland Waters Directorate.

Gregor, D. J. and W. Rast. 1982. Simple Trophic State Classification of the Canadian Nearshore Waters of the Great Lakes. Water Resources Bull. 18(4):565-573.

Heathcote, I. W. 1979. Nanticoke Water Chemistry, 1978. Toronto: Ontario Ministry of the Environment.

Heathcote, I. W. 1981. Major Physical Features of Long Point Bay and its Watershed. J. Great Lakes Res. 7(2):89-95.

Heathcote, I. W., Weiler, R. R., and J. W. Tanner. 1981. Lake Erie Nearshore Water Chemistry at Nanticoke, Ontario, 1969-1978. J. Great Lakes Res. 7(2):130-135.

Herricks, E. E., Schaeffer, D. J. and J. C. Kapsner. 1985. Complying with NPDES Permit Limits: When is a Violation a Violation? J. Water Pollut. Control Fed. 57(2):109-115.

Hirsch, R.M. and J.R. Slack 1984. A nonparametric trend test for seasonal data with serial dependence. Water Resources Res. 20(6): 727-732.

Hirsch, R.M., J.R. Slack and R.A. Smith 1982. Techniques of trend analysis for monthly water quality data. Water Resources Res. 18(1): 107-121.

Hopkins, G.J. and C. Lea. 1982. A Ten-Year Study of Phytoplankton Biomass and Composition in the Nanticoke Region of Long Point Bay, Lake Erie. J. Great Lakes Res. 8(3):428-438.

International Joint Commission. 1979. Great Lakes Water Quality 1978, Appendix B. Surveillance Subcommitee Annual Report to the Implementation Committee of the Great Lakes Water Quality Board, July 1979.

International Lake Erie Water Pollution Board; International Lake Ontario - St. Lawrence River Water Pollution Board. 1969. Pollution of Lake Erie, Lake Ontario and the International Section of the St. Lawrence River. Report to the International Joint Commission.

Jeffs, D. N. 1981. Introduction to the Special Issue on the Long Point Bay Study. J. Great Lakes Res. 7(2):77-80.

Kendall, M. 1975. Rank Correlation Methods. Fourth Edition London: Charles Griffin.

Knuth, D.E. 1969. The Art of Computer Programming. Reading, Massachusetts: Addison-Wesley.

Kruskal, W.H. and W.A. Wallis 1952. Use of ranks on one-criterion variance analysis. American Statistical Association, 47: 583-621.

Mann, H.B. 1945. Nonparametric tests against trend. Econometrica, 13: 245-259.

McGirr, D. J. 1974. Interlaboratory Quality Control Study No. 10, Turbidity and Filterable and Nonfilterable Residue. Report Series No. 37. Burlington, Ontario: Environment Canada, Inland Waters Directorate.

McNeil, D.R. 1977. Interactive Data Analysis. New York: John Wiley.

Ontario Ministry of the Environment. 1981. Outlines of Analytical Methods. Toronto: Ministry of the Environment Laboratory Services Branch.

Ontario Ministry of the Environment. 1983. Handbook of Analytical Methods for Environmental Samples. Toronto: Ministry of the Environment Laboratory Services and Applied Research Branch.

Ontario Ministry of the Environment. 1984. Water Management - Goals, Policies, Objectives and Implementation Procedures of the Ministry of the Environment. Toronto: Ministry of the Environment.

Palmer, M. D. 1968. Required Density of Water Quality Sampling Stations at Nanticoke, Lake Erie, Toronto: Ontario Water Resources Commission.

Palmer, M. D. 1970. Water Chemistry, Nanticoke Area, Lake Erie, 1969. Toronto: Ontario Water Resources Commission.

Palmer, M. D. 1971. Water Chemistry in the Nanticoke Area of Lake Erie; 1969 - 1971. In: Nanticoke: A Preoperational Report, Vol 2, Water Chemistry. Toronto: Ontario Ministry of the Environment.

Palmer, M, D. 1972. Water Chemistry in the Nanticoke Area of Lake Erie, 1972. Toronto: Ontario Ministry of the Environment.

Pitman, E.J.G. 1939. A note on normal correlation. Biometrika, 31: 9-12.

Polak, J. 1975. Nanticoke Water Chemistry, 1974 Report. Toronto: Ontario Ministry of the Environment.

Polak, J. 1977. Nanticoke Water Chemistry, 1975. Toronto: Ontario Ministry of the Environment.

Polak, J. 1978a. Nanticoke Water Chemistry, 1976. Toronto: Ontario Ministry of the Environment.

Polak, J. 1978b. Nanticoke Water Chemistry, 1977. Toronto: Ontario Ministry of the Environment.

Polak, J. and D. H. Kennedy. 1975. Nanticoke Water Chemistry, 1973. Toronto: Ontario Ministry of the Environment.

Rathke, D. E. and C. J. Edwards. 1985. A Review of Trends in Lake Erie Water Quality with Emphasis on the 1978-1979 Intensive Survey. Report to the Surveillance Work Group. Windsor, Ontario: International Joint Commission.

Sachs, L. 1984. Applied Statistics, A Handbook of Techniques. Second Edition, New York: Springer-Verlag.

Schwarz, G. 1978. Estimating the dimension of a model. Annals of Statistics 6(2): 461-464.

Sonzogni, W. C, Richardson, W., Rodgers, P. and T. J. Monteith. 1983. Chloride Pollution of the Great Lakes. J. Water Pollut. Control Fed. 55(5):513-521.

Tanner, J. W. 1981. Nanticoke Water Chemistry, 1979. Toronto: Ontario Ministry of the Environment.

Tukey, J.W. 1977. Exploratory Data Analysis. Reading Massachusetts: Addison-Wesley.

Weiler, R. R. and I. W. Heathcote. 1979. Nanticoke Water Chemistry, Summary Report, 1969 - 1978. Toronto: Ontario Ministry of the Environment.

Weiler, R. R. and R. MacGregor. 1984. The Aquatic Environment of Long Point Bay in the Vicinity of Nanticoke on Lake Erie. Toronto: The Nanticoke Environmental Committee.

Wilcoxon, F. 1945. Individual comparisons by ranking methods. Biometrics 1: 80-83.

TD
227.E75
O57
1986

Nanticoke water quality study
1969-1983 : main report /

24262